COMPUTATIONAL STUDIES OF ENERGETIC ORGANIC MOLECULES

by

Peter Politzer and Jane S. Murray

Prepared for Publication

in

Department of Chemistry
University of New Orleans
New Orleans, LA 70148

December 27, 1993

DTIC QUALITY INSPECTED 8

DTIC
S ELECTE
E JAN 12 1994 **D**

Accesion For		
NTIS CRA&I	☒	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By		
Distribution /		
Availability Codes		
Dist	Avail and / or Special	
A-1		

AD-A274 726

94 1 10 136

94-01167

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 12-27-93	3. REPORT TYPE AND DATES COVERED Preprint of chapter for publication

4. TITLE AND SUBTITLE

Computational Studies of Energetic Organic Molecules

5. FUNDING NUMBERS

C N00014-91-J-4057

Dr. Richard S. Miller

R&T Code 4131D02

6. AUTHOR(S)

Peter Politzer and Jane S. Murray

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of New Orleans
Department of Chemistry
New Orleans, Louisiana 70148

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
Code 332PE
800 N. Quincy Street
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for pulic release.
Unlimited distribution.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

We discuss first-principles calculations that have been carried out for organic energetic molecules of the following types: a) nitroaromatics; b) aliphatic and alicyclic nitramines; c) highly strained cagelike systems; and d) high-nitrogen-content molecules. Our scope includes both *ab initio* molecular orbital methods and also density functional procedures, with a specific emphasis on the understanding of factors influencing shock/impact sensitivities and relative stabilities. For each class of compounds mentioned above, we discuss structural and electronic properties, followed generally by a review of calculations relating to the decompositions of some specific members of these classes. Our discussion of sensitivity and its relationship to molecular properties focuses upon general correlations that exist within separate categories of compounds, e.g. nitroaromatics and nitramines, and upon exceptions to these relationships which suggest that other factors may play key roles in specific instances. In the area of high-nitrogen-content molecules, the presence of localized N-N bonds appears to be a factor favoring instability/high sensitivity.

14. SUBJECT TERMS

nitroaromatics; aliphatic nitramines; alicyclic nitramines; cagelike systems; high-nitrogen-content molecules; ab initio; density functional method; shock/impact sensitivities

15. NUMBER OF PAGES

48

16. PRICE CODE

| 17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

I. Introduction

A. General:

Energetic materials are substances containing metastable molecules capable of undergoing very rapid highly exothermic reactions [Iyer and Slagg, 1988]. They are generally divided into three major classes: explosives, propellants and pyrotechnics [Meyer, 1987; Iyer and Slagg, 1988]. Our focus in this chapter will be primarily on the first two categories (explosives and propellants).

The study of energetic systems by theoretical methods has accelerated dramatically over the course of the last decade and has provided considerable insight into the understanding of factors affecting their behavior. In this chapter we will discuss first-principles calculations that have been carried out for energetic molecules of a variety of structural types, including: a) nitroaromatics; b) aliphatic and alicyclic nitramines; c) highly strained cagelike systems; and d) high-nitrogen-content molecules. Our scope will include *ab initio* molecular orbital methods and also density functional procedures. A specific emphasis will be the understanding of factors influencing shock/impact sensitivities and overall stabilities.

Before launching our discussions of calculations carried out for the different structural types, it is useful to point out a molecular feature that is common to all of them, namely a relatively high degree of charge separation. For example, a component of many currently-used and proposed energetic molecules (e.g. **1** - **6**) is the NO_2 group [Meyer, 1987; Iyer and Slagg, 1988;
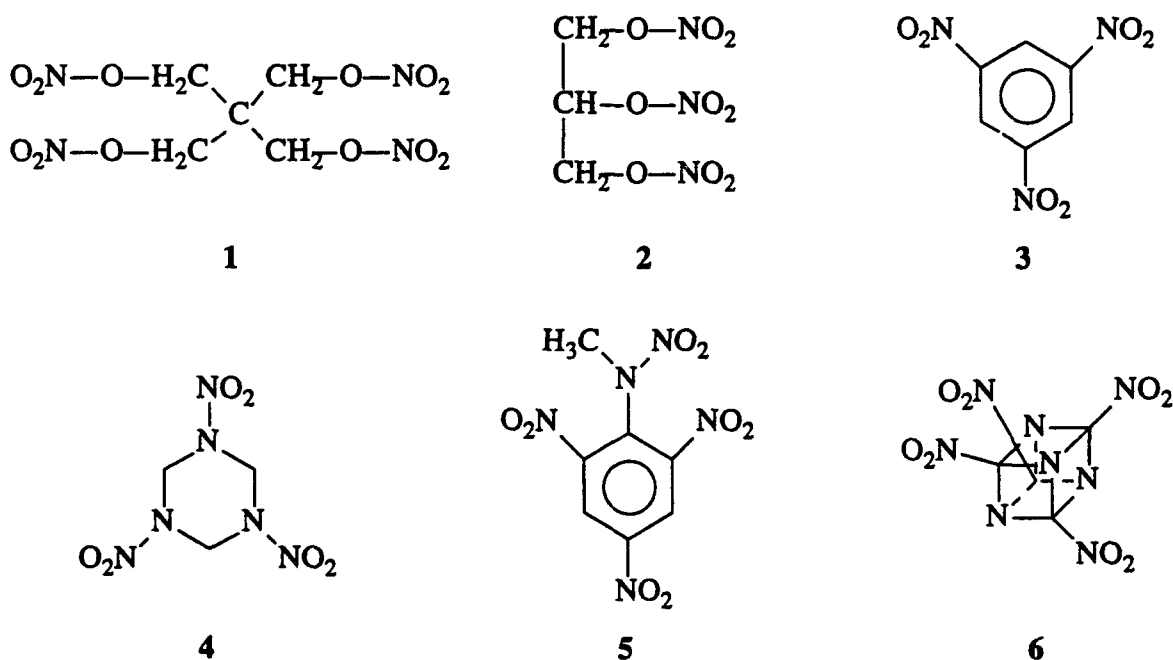
Bulusu, 1990]. Its presence introduces significant charge separation, or local polarity, even in a molecule which has a zero dipole moment, due to the nitro group's strongly electron-attracting

tendencies [Exner, 1988]. Thus, molecules such as **1 - 6** can be viewed as possessing relatively high degrees of local polarity. We will discuss the significance of this for energetic molecules in later sections.

B. Structure-Sensitivity Relationships:

A continuing major theme of energetic materials research has been the effort to better understand the relationship between the molecular structures of energetic compounds and their sensitivities to specific stimuli, such as impact and shock. Indeed, this has been the driving force for many computational studies. A key long range goal is the design and manufacture of less sensitive, less vulnerable munitions.

Sensitivity has been defined as the ease with which a substance subjected to external stimuli, such as shock, impact or heat, can be made to undergo detonation [Iyer and Slagg, 1988]. An ideal explosive would be one which achieves high performance, but is insensitive enough to permit safe handling; however it should not be so insensitive that detonation becomes difficult or impractical.

Many kinds of sensitivity have been identified in terms of the nature of the stimulus causing detonation [Iyer and Slagg, 1988]; some of these include heat, friction, impact, shock and electrostatic charge. Two of the most commonly used measures of an explosive's tendency to detonate are impact and shock sensitivity. Impact tests (of which there are several, similar in principle but differing in detail) involve subjecting a sample to the impact of a standard weight falling from varying heights [Kamlet and Adolph, 1979]; the sensitivity is inversely proportional to the height at which there is a 50% probability of causing an explosion (called impact drop height or h_{50}). Shock sensitivity is often measured by a standard small scale gap test [Storm, Stine and Kramer, 1990], and is interpreted as being directly proportional to the maximum gap width through which a given shock wave generated by another explosive (e.g. RDX) will detonate the compound 50% of the time.

Kamlet and Adolph's (1979) stoichiometric means of assessing impact sensitivity through correlations with "oxygen balance" has been widely applied in the area of energetic materials research. The term "oxygen balance", or OB_{100}, refers to the amount of oxygen available for the combustion of the C and H atoms in a molecule to CO and H_2O, and is defined for C-H-N-O compounds in eq. (1).

$$OB_{100} = \frac{100 \ (2n_O - n_H - 2n_C - 2n_{COO})}{M} \tag{1}$$

n_O, n_H and n_C represent the numbers of atoms of the respective elements in the molecule, n_{COO} is the number of carboxyl groups, and M is the molecular weight. Kamlet and Adolph demonstrated that for families of high energy molecules with similar decomposition mechanisms (e.g. trinitro-

methyl, N-nitro and gem-dinitro compounds and nitroaromatics with and without α-C-H linkages) there are approximately linear relationships between $\log h_{50}$ and OB_{100}. In these correlations, $\log h_{50}$ increases as OB_{100} decreases for any one family of molecules; the more impact-sensitive explosives are those with the more positive OB_{100} values. Stine [1989] has since proposed a sensitivity index based on the geometric properties of a regular tetrahedron which has been shown to correlate with OB_{100} values [Storm, Stine and Kramer, 1989].

Although such stoichiometric relationships have proven to be quite useful for a number of classes of compounds, taken separately, they do not allow one to distinguish between structural isomers, which can have quite different sensitivities. This consideration has prompted a variety of investigations aimed at elucidating the relationship of molecular structure to impact/shock sensitivity. Considerable attention has been given to the idea of a key "trigger" linkage in explosives, as was proposed by Kamlet and Adolph [1981]. In light of numerous studies, both theoretical and experimental, supporting the importance of $C\text{-}NO_2$ and $N\text{-}NO_2$ bonds in determining the sensitivities of many nitroaromatics, nitroaliphatics and nitramines, it is the general consensus that in many such molecules, $C\text{-}NO_2$ or $N\text{-}NO_2$ bonds are the actual "triggers".

Table 1 lists the sensitivities for some common explosives. For the limited number of compounds included in the table, it can be seen that the nitrate esters **1** and **2** and the nitramines **4** (RDX) and **7** (HMX) are more sensitive to shock and impact than the nitroaromatics (**3, 5** and **8 - 10**). The sensitivities of the trinitroaromatics cover a relatively wide range and appear to be highly dependent upon the substituents on the aromatic ring. In this chapter, factors affecting the impact and/or shock sensitivities of explosives will be examined separately for different types of molecules, when possible, and later from a broader perspective, encompassing all of them.

7　　　　**8**　　　　**9**　　　　**10**
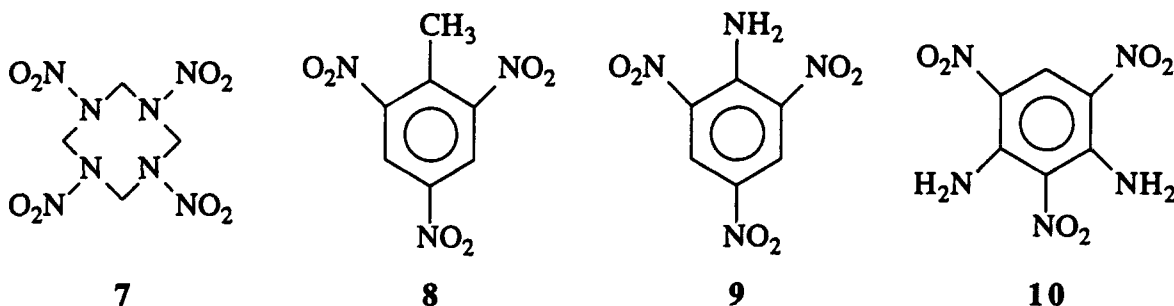
II. Methodologies

A. General:

The calculations to be discussed in this chapter involve primarily *ab initio* molecular orbital and density functional procedures. Theoretical background and computational details pertaining to these two first-principles approaches are reviewed elsewhere [*ab initio*: Hehre, Radom, Schleyer and Pople, 1986; Hinchliffe, 1988; density functional: Parr and Yang, 1989; Kryachko and Ludeña, 1990; Labanowski and Andzelm, 1991]. The emphasis in this chapter is upon the results

of these computations. There have also been semi-empirical studies of energetic molecules (e.g. Alster, Slagg, Dewar, Ritchie and Wells, 1981; Turner and Davis, 1984), and some of these will be mentioned.

B. Structures:

A complete theoretical determination of the equilibrium structure of a molecule involves minimization of its energy with respect to each independent geometrical parameter [Hehre, Radom, Schleyer and Pople, 1986], resulting in an "optimized" structure. The resulting geometry is necessarily somewhat dependent upon the methodology and basis set used to perform the optimization.

Table 2 compares some calculated *ab initio* Hartree-Fock (HF), post-Hartree-Fock and density functional structural data with experimental values (when available) for several small molecules which can be viewed as building blocks of larger explosives. Several significant trends emerge which are important in selecting computational procedures and basis sets for geometry optimizations of molecules containing $C-NO_2$ and $N-NO_2$ linkages. (The term "basis set" refers to the functions used to build up the molecular orbitals. The ones that will be mentioned are designated as STO-3G, 3-21G and 6-31G*; these increase in size and flexibility in the order given.) Thus, although HF/STO-3G structures are often quite satisfactory, Table 2 shows that N-O bond lengths obtained at this computational level are too large by about 0.05 Å. The HF/3-21G N-O distances are much better, being overestimated by approximately 0.02 Å, while the HF/6-31G* tend to be underestimated by about the same amount. The inclusion of electron correlation via post-Hartree-Fock or density functional procedures is seen to yield N-O bond lengths that are generally comparable to the HF/3-21G.

Thus, Table 2 shows that satisfactory nitro group geometries can be computed both with and without the inclusion of electron correlation. In the framework of *ab initio* HF theory, it is advisable to carry out geometry optimizations with the more flexible basis sets (e.g. 3-21G or 6-31G*). The effect of computational method and level upon the structural features of high-nitrogen-content molecules will be discussed in detail in a later section.

C. Energies:

Calculated energies can be used to determine relative stabilities of structural isomers, reaction energetics and isodesmic reaction energies. Isodesmic reactions provide insight into anomalous energy effects in molecules [Hehre, Ditchfield, Radom and Pople, 1970; Hehre, Radom, Schleyer and Pople, 1986]. They are hypothetical chemical processes in which the number of bonds of each formal type remains the same on each side of the equation, but their mutual relationships are changed. For example, an isodesmic reaction involving cyclopropane (C_3H_6) is: $3C_2H_6 \rightarrow C_3H_6 + 3CH_4$. The ΔE values for reactions such as this are interpreted as

representing any deviations from bond energy additivity and therefore indicative of any anomalous energetic effects associated with the molecule being investigated, e.g. strain, resonance stabilization, steric effects, etc. ($\Delta E < 0$ indicates the presence of stabilizing factors, while $\Delta E > 0$ implies destabilization.)

D. Reaction Energetics:

The elucidation of the decomposition mechanisms of energetic molecules is of considerable importance, both for understanding how the stored energy is released and also for seeking to improve the stabilities of such systems. Theoretical investigations of reaction energetics complement experimental studies in this area. Several of computational studies will be discussed, in which the interest was primarily in obtaining reaction energies and/or activation barriers, and which were carried out with either *ab initio* or density functional procedures.

E. Molecular Properties:

1. *The Electrostatic Potential, V(r):*

The electrostatic potential is a real physical property that reflects the net electrical effect of the nuclei and electrons of a molecule at any point in space $\mathbf{r}$; it is defined rigorously by eq. (2).

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')\, d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \qquad (2)$$

Z_A is the charge on nucleus A, located at $\mathbf{R}_A$, and $\rho(\mathbf{r})$ is the electronic density function, which we determine computationally. The electrostatic potential is well-established as an effective guide to chemical reactivity [Scrocco and Tomasi, 1978; Politzer and Daiker, 1981; Politzer and Truhlar, 1981; Politzer and Murray, 1991]. In those regions where $V(\mathbf{r})$ is negative, the effects of the electrons dominate and these are accordingly attractive sites for the initial attack of electrophiles. Predicting sites reactive toward nucleophiles is less straightforward due to the effects of the nuclei, but we have shown that when $V(\mathbf{r})$ is plotted on the molecular surface, the regions of most positive potential do allow predictions for nucleophilic processes [Sjoberg and Politzer, 1990; Politzer and Murray, 1991; Murray and Politzer, 1991].

2. *Atomic Charges and V_{mid}:*

We have recently modified and extended an earlier relationship between impact sensitivity of nitroaromatics and V_{mid}, the electrostatic potential at the midpoint of the $C-NO_2$ bonds [Owens, Jayasuriya, Abrahmsen and Politzer, 1985; Murray, Lane, Politzer and Bolduc, 1990] ; the latter is approximated by

$$V_{mid} = \frac{Q_C}{0.5\,R} + \frac{Q_N}{0.5\,R} \qquad (3)$$

Q_C and Q_N are the atomic charges on the carbon and nitrogen, obtained from the Mulliken population analysis of the SCF-MO wave function [Mulliken, 1955]; R is the C-N bond length in bohrs. The relationship between nitroaromatic impact/shock sensitivities and V_{mid} will be discussed in a later section.

3. *The Average Local Ionization Energy, $\bar{I}(r)$:*

We have also introduced another calculated property that is an effective tool for analyzing certain aspects of chemical reactivity. This is the average local ionization energy, $\bar{I}(r)$, defined by eq. (4) [Sjoberg, Murray, Brinck and Politzer, 1990]:

$$\bar{I}(r) = \sum_i \frac{\rho_i(r)\,|\varepsilon_i|}{\rho(r)} \qquad (4)$$

$\rho_i(r)$ is the electronic density of the ith molecular orbital at the point r, ε_i is the orbital energy, and $\rho(r)$ is the total electronic density. $\bar{I}(r)$ can be interpreted as the average amount of energy required to remove an electron at any point r in the space of the molecule. We have shown that $\bar{I}(r)$ plotted on molecular surfaces is a very good indicator of sites for electrophilic attack; these are where $\bar{I}(r)$ has its lowest values, indicating the most easily removed and hence most reactive electrons [Sjoberg, Murray, Brinck and Politzer, 1990; Brinck, Murray and Politzer, 1991]. For example, for a series of monosubstituted benzenes, the surface $\bar{I}(r)$ minima ($\bar{I}_{S,min}$) provide a quantitative measure of the activating/deactivating and the directing tendencies of the various substituents, and also correlate well with the Hammett constants σ_p and/or σ_m [Sjoberg, Murray, Brinck and Politzer, 1990]. Surface $\bar{I}(r)$ can also be used successfully to predict the strengths of acids [Brinck, Murray, Politzer and Carter, 1991; Brinck, Murray and Politzer, 1991]. For 24 acids of various types (carboxylic, inorganic, etc.), there is an excellent linear relationship between the experimentally-determined pK_a of each acid and the $\bar{I}_{S,min}$ of its conjugate base. It is particularly noteworthy that these relationships are between a measured solution property and a gaseous phase calculated one.

III. Nitroaromatics

Due to the importance of nitroaromatics as a class of explosives, there has been considerable interest in their properties, mechanisms of decomposition, and factors affecting their sensitivities. In this section we will begin with a discussion of structural and electronic properties of nitroaromatics, followed by a review of calculations relating to the decomposition of some

members of this class. Finally we will survey relationships found between calculated properties and the impact/shock sensitivities of these compounds.

Certainly a relevant feature of aromatics in general and one to which we will refer again is the influence that any particular substituent or group of substituents can have upon the aromatic ring. This is presumably due to the presence of the polarizable π electrons and the possibility of conjugation, and is reflected in the fact that both resonance and inductive effects play prominent roles in determining the distributions of charge in these systems. In this context, it is noteworthy that the role of resonance is determined by difference [Exner, 1988], often using a general relationship of the type $\sigma_p - \sigma_I = \sigma_R$, where the Hammett constant σ_p is defined in terms of *para*-substituted aromatics (e.g. benzoic acids), for which resonance interactions by resonance donors can be quite significant, and σ_I is determined independently for series such as substituted acetic acids for which inductive effects predominate.

Nitrobenzene (**11**) can be described in terms of resonance structures such as **11a** - **11e**. A number of theoretical studies have analyzed the inductive and resonance (i.e. **11c** - **11e**)

| **11** | **11a** | **11b** | **11c** | **11d** | **11e** |
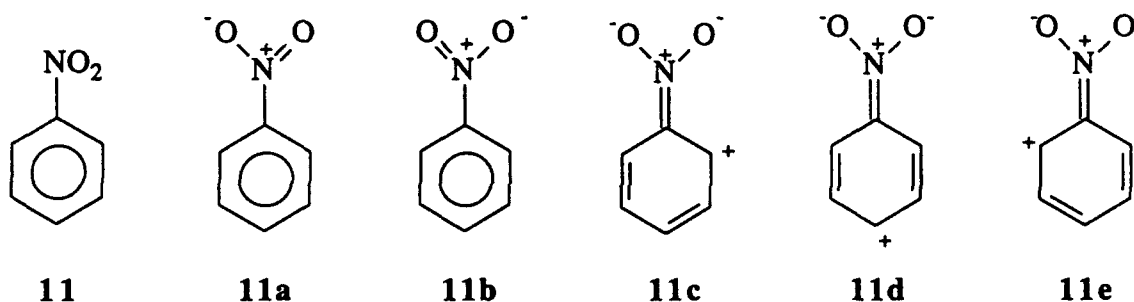
contributions to the strongly electron-withdrawing tendency of the NO_2 [Lipkowitz, 1982; Hiberty and Ohanessian, 1984; Politzer, Lane, Jayasuriya and Domelsmith, 1987; Ritchie, 1988]. The general consensus is that there is only a small degree of conjugation between the nitro group and the aromatic ring in nitrobenzene. This is consistent with the well-established inductive and resonance substituent constants σ_I and σ_R of the nitro group (0.67 and 0.10, respectively [Exner, 1988]), and with the relatively low rotational barrier around the $C-NO_2$ bond in nitrobenzene, around 3 kcal/mole [Høg, Nygaard and Sorensen, 1971; Correl, Larsen and Pedersen, 1980]. Even in the case of the observed "through-resonance" interactions in some *para*-substituted nitrobenzenes [Hammett, 1970], such as *para*-nitroaniline, **12**, there is experimental [Lipkowitz, 1982] and theoretical [Hiberty and Ohanessian, 1984] evidence that **12c** is the dominant resonance contributor.

12a **12b** **12c**
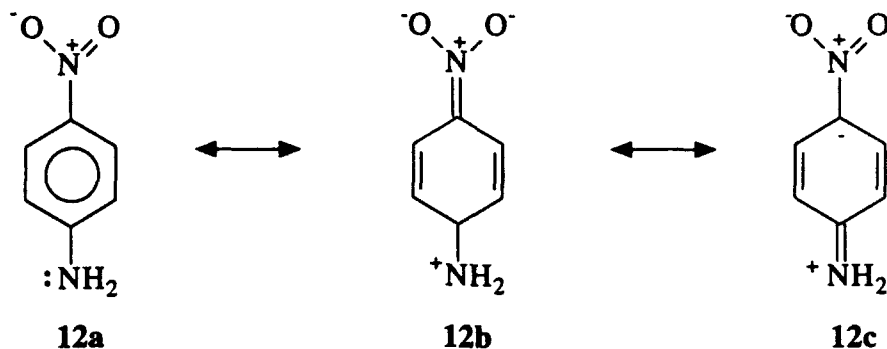
The strongly electron-withdrawing nitro group significantly deactivates the ring an aromatic ring toward electrophilic aromatic substitution [Allinger, Cava, DeJongh, Johnson, Lebel and Stevens, 1971]. This is reflected in the electronic density distributions of nitroaromatics and also in related properties such as the electrostatic potential $V(r)$ and the average local ionization energy $\bar{I}(r)$. For example, the regions of negative electrostatic potential that are characteristically found above and below the planes of the benzene ring (Figure 1), and are attributed to the π electrons, are completely eliminated upon the substitution of a single nitro group (Figure 2) [Politzer, Abrahmsen and Sjoberg, 1984].

The deactivating *meta*-directing influence of NO_2 upon electrophilic aromatic substitution can be predicted from the calculated average local ionization energy $\bar{I}(r)$ of nitrobenzene plotted on the molecular surface [Sjoberg, Murray, Brinck and Politzer, 1990; Murray, Brinck and Politzer, 1992]. The locations of the $\bar{I}_{S,min}$ above the *meta* positions indicate that these are the positions where the most reactive electrons are found, and thus are the most favorable sites for electrophilic attack. The magnitudes of these $\bar{I}_{S,min}$ are greater than those of benzene, consistent with the deactivating influence of the NO_2. As mentioned earlier, we have shown that the $\bar{I}_{S,min}$ above the *para* and/or *meta* positions of a series of substituted benzenes correlate well with the respective Hammett constants σ_p and/or σ_m. This permits us to predict Hammett constants for substituents for which these are not known, e.g. the NF_2 and $N(NO_2)_2$ groups [Sjoberg, Murray, Brinck and Politzer, 1990; Politzer, Murray, Seminario and Miller, 1992].

The commonly used nitroaromatic explosives are benzene derivatives which contain three or more nitro groups (e.g see 5 - 10 in Table 1). The sensitivities of these compounds cover a wide range [Kamlet and Adolph, 1979; Storm, Stine and Kramer, 1990], and have been shown to be highly dependent upon the natures of the additional substituents upon the aromatic ring [Owens, 1984; Owens, Jayasuriya, Abrahmsen and Politzer, 1985; Murray, Lane, Politzer and Bolduc, 1990]. Except for the sensitizing effect of the OH group [Kamlet and Adolph, 1979], which we will discuss subsequently, electron-donating substituents (e.g. NH_2, OCH_3 and CH_3) are generally desensitizing; this is exemplified by the aminotrinitrobenzenes (e.g. see 9 and 10 in Table 1). In contrast, electron-withdrawing groups (including another NO_2) increase sensitivity. Owens [1984],

for example, has demonstrated for a group of eleven trinitroaromatics that impact sensitivity correlates inversely with the total donating ability of the non-nitro substituents on the ring.

One interpretation of these observations is that resonance donors strengthen to some degree the C-NO$_2$ bonds, as is shown below for 2,4,6-trinitroaniline (9):


9a   **9b**

9c   **9d**
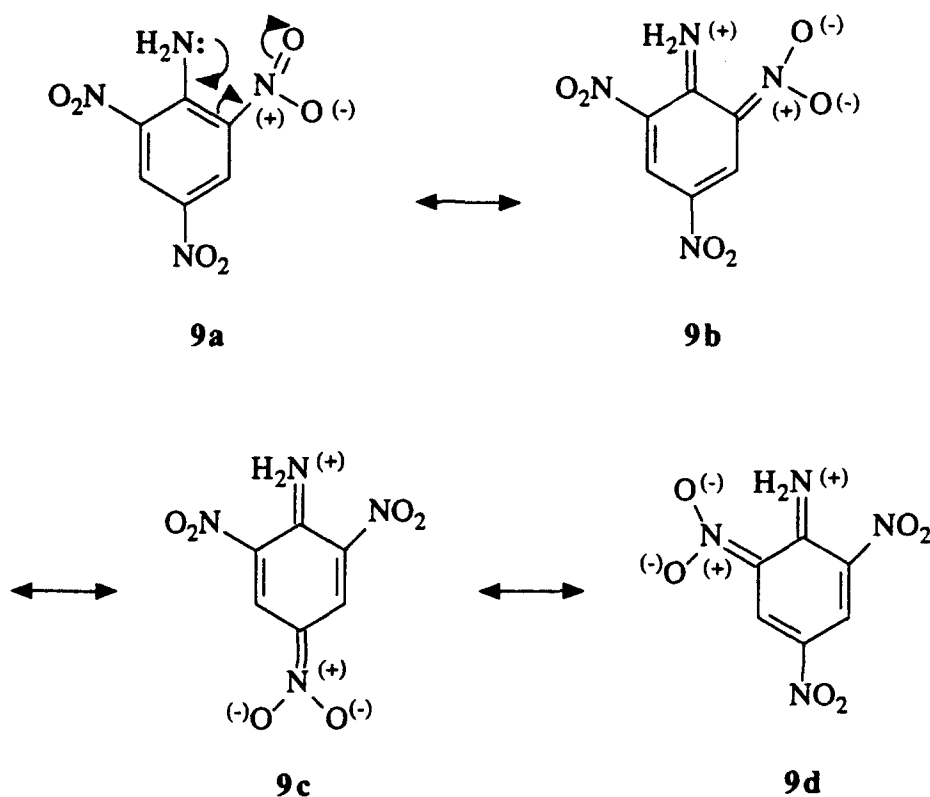
As we have pointed out earlier, however, the degree of resonance electron-withdrawal by the nitro group into the C-NO$_2$ bond region is believed to be small, even with strong electron donors present, and the resonance structures **9b** - **9d** may play only a minor role.

Consistent with an emphasis upon C-NO$_2$ bond strength are the relationships found between impact sensitivity and V_{mid}, the electrostatic potential at the midpoint of the C-NO$_2$ bond as approximated from atomic charges by eq. (2) [Owens, Jayasuriya, Abrahmsen and Politzer, 1985; Murray, Lane, Politzer and Bolduc, 1990]. In general, impact sensitivity increases as the largest V_{mid} of the trinitroaromatic molecule, $V_{mid,max}$, increases. In view of the relationship between eq. (2) and a bond energy expression developed by Fliszar (1980), it can be inferred that the instability of an individual C-NO$_2$ linkage may be a key factor in initiating decomposition induced by impact. The presence of electron-donating groups such as NH$_2$, OCH$_3$ and CH$_3$ tends to diminish $V_{mid,max}$, suggesting that these may reduce the instabilities of the C-NO$_2$ linkages relative to those of trinitrobenzene.

The OH group is an exception to this pattern. Even though it is electron-donating, hydroxynitroaromatics such as **13** - **15** have anomalously high sensitivities. Politzer, Seminario

and Bolduc [1989] have investigated the possibility that this may be due to nitronic acid formation. Using a model system, o-nitrophenol (16), the proton transfer to form the nitronic acid 17, shown in eq. (5), was predicted (at the HF/3-21G level) to occur to a small but significant extent. It was suggested that the formation of unstable nitronic acids, accompanied by the disruption of
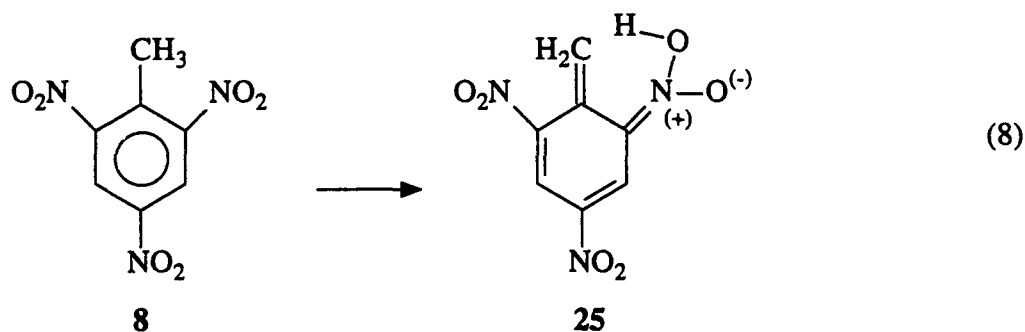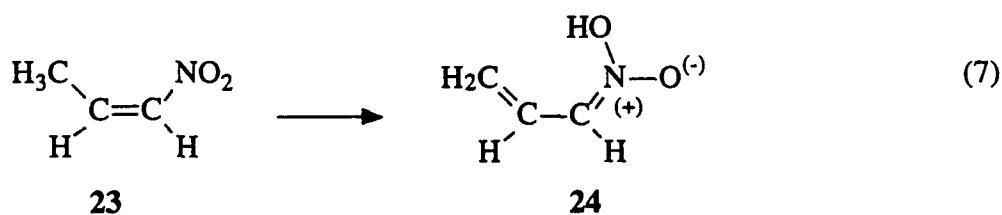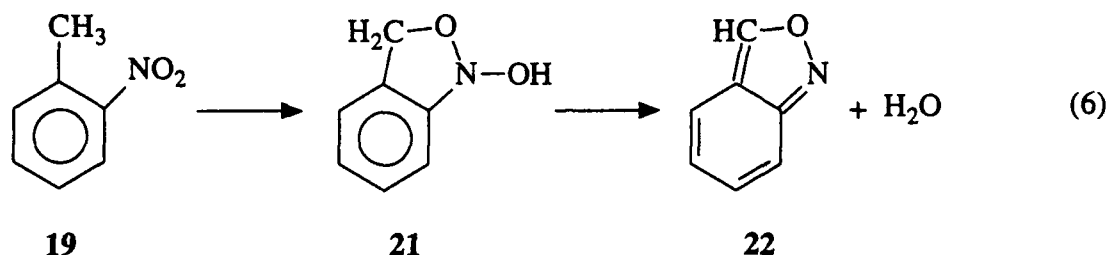

13

14

15

16

17

(5)
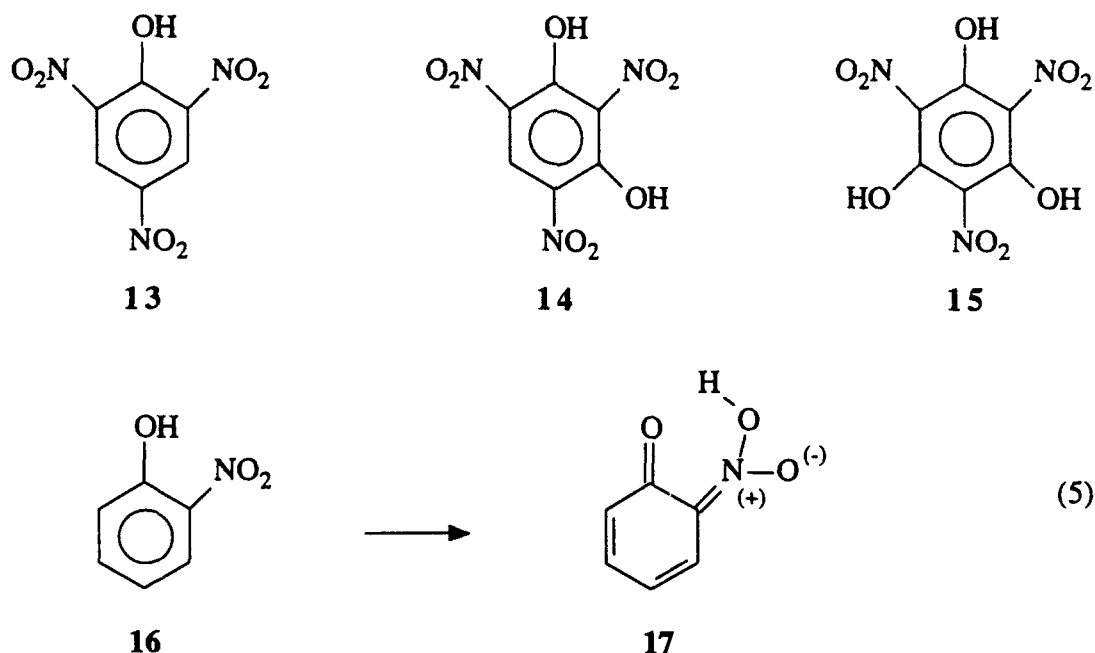
aromaticity, may contribute to the observed sensitizing effects of hydroxyl substituents in nitroaromatics [Politzer, Seminario and Bolduc, 1989].

In a later computational study [Murray, Lane, Politzer, Bolduc and McKenney, 1990], hydrogen transfer reactions for two widely-studied nitroaromatic explosives, 2,4,6-trinitro-toluene (8, TNT) and 1,3,5-triamino-2,4,6-trinitrobenzene (18, TATB), were investigated, again using

18

19

20
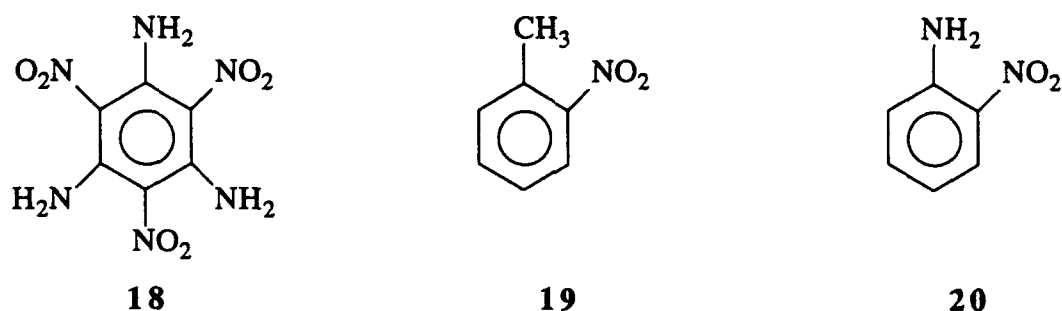
model systems: o-nitrotoluene (19) and o-nitroaniline (20). The objective was to gain insight into the very different thermal, shock and impact sensitivities of 8 and 18 [Kamlet and Adolph, 1982]. TNT is thermally labile, self-igniting at temperatures between 200 and 210° C, and has intermediate impact and shock sensitivities. TATB, on the other hand, is stable to temperatures well above 300 ° C and is so insensitive to impact and shock that it is impractical as an explosive.

Our results for *o*-nitrotoluene (**19**) indicate that intramolecular hydrogen transfer to form a bicyclic tautomer **21** is highly favored thermodynamically at the HF/3-21G level, as is the further loss of water to form anthranil **22** [eq. (6)]. An interesting feature of these results is that for the model system **19**, we do not find a nitronic acid tautomer analogous to **17**, but rather the thermo-dynamically favored bicyclic systems **21** and **22**. In this context, it is noteworthy that an earlier semi-empirical investigation of the thermal decomposition of TNT using 1-nitropropene (**23**) as a model [Turner and Davis, 1984], and also at the *ab initio* HF/STO-3G level using TNT itself [Cox and Hillier, 1988], found the formation of the nitronic acids **24** and **25** to be thermodynamically highly unfavorable [eqs. (7) and (8)].

$$\text{19} \longrightarrow \text{21} \longrightarrow \text{22} + H_2O \tag{6}$$

$$\text{23} \longrightarrow \text{24} \tag{7}$$

$$\text{8} \longrightarrow \text{25} \tag{8}$$

Evidence of the formation of an intramolecular, five-membered ring analogous to **22** has been reported in low-temperature studies of TNT by Rogers [1967] and by Dacon *et al* [1970]. We have suggested from our results for the model system **19** that energy produced by forming products such as **21** and **22** could help to stimulate further reactions [Murray, Lane, Politzer, Bolduc and McKenney, 1990]. This idea is consistent with experimental results indicating that a product of TNT resulting from a methyl C-H bond rupture accumulates to a threshold level and then catalytically initiates its continuing exothermic thermochemical decomposition [Shackelford, Beckmann and Wilkes, 1977].

For *o*-nitroaniline (**20**), tautomerization to a nitronic acid was also found to be thermodynamically unfavorable at the HF/3-21G level, while conversion to benzofurazan **26** with the elimination of water [eq. (9)] was calculated to be thermochemically nearly neutral. Five-membered ring formation giving furazans (analogous to **26**) has been reported in thermal decomposition and underwater shock and impact studies of TATB (**18**) [Sharma, Hoffsomer, Glover, Coffey, Santiago, Stolovy and Yasuda, 1983; Sharma, Forbes, Coffey and Liddiard, 1987] . It has been predicted that the steps producing furazan derivatives of TATB [e.g. **27** in eq. (10)] are thermodynamically nearly neutral, and this has been suggested as helping to account for its very low sensitivity [Storm, Stine, and Bulusu, 1990]. Our HF/3-21G results for the model system **20** are consistent with this view.

20   **26**   (9)

18   **27**   (10)
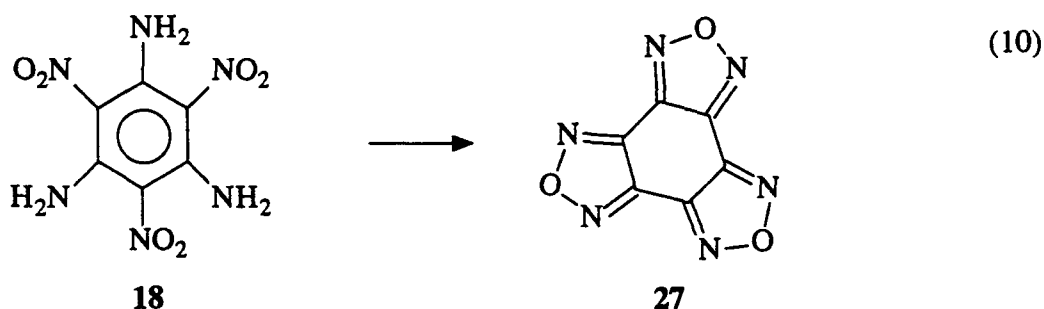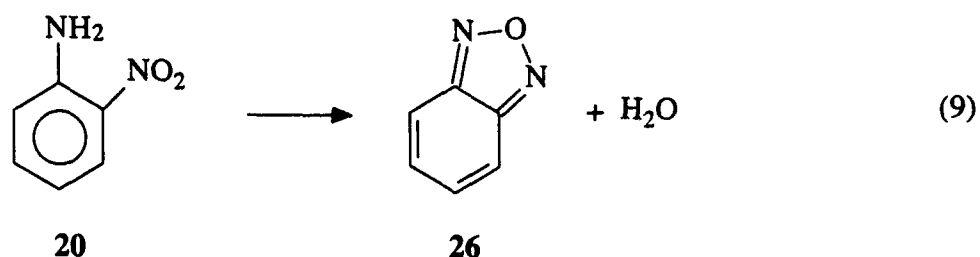
As we have mentioned earlier, the presence of the nitro group in an organic molecule introduces some degree of charge separation, or local polarity, due to the strongly electron-attracting power of the NO_2; this occurs even if the symmetry of the molecule is such that the overall dipole moment is zero. The electrostatic potentials shown in Figs. 1 and 2 for benzene and nitrobenzene provide some indications of the charge separation within these two molecules. Indeed $V(\mathbf{r})$, defined by eq. (2), is a physical manifestation of the distribution of electronic and nuclear charge within a system.

To provide a quantitative measure of the local polarity that may be present even in a zero-dipole-moment molecule, we have recently introduced a polarity index Π, defined in terms of the electrostatic potential $V(\mathbf{r})$ by eq. (11) [Brinck, Murray and Politzer, 1992]:

$$\Pi = \frac{1}{A} \int_{S} \left| V(\mathbf{r}) - \bar{V}_S \right| dS \tag{11}$$

The integral represents the total amount by which the electrostatic potential on the molecular surface deviates from its average value, $\bar{V}_S$; this is divided by the surface area A in order to permit comparisons between molecules of different sizes.

A computationally practical form of eq. (11) is given by eq. (12),

$$\Pi = \frac{1}{n} \sum_{i=1}^{n} \left| V_i(r) - \bar{V}_S \right| \tag{12}$$

where $V_i(r)$ is the potential at the ith point on the surface and $\bar{V}_S = \frac{1}{n} \sum_{i=1}^{n} V_i(r)$. As n increases, eq. (12) approaches eq. (11). We have proposed eq. (12) as the working formula for Π, which can be viewed as the average deviation of the electrostatic potential on the molecular surface [Brinck, Murray and Politzer, 1992]. We have computed Π for molecules of a variety of types, and demonstrated its relationship to an empirical polarity-polarizability parameter and also to the dielectric constant, an experimentally-determined bulk property.

Table 3 lists our calculated Π values for a variety of molecules (including nitrobenzene, p-dinitrobenzene and a number of other monosubstituted aromatics), computed at the HF/STO-5G level on molecular surfaces defined in accordance with Bader $et\ al$ [1987] by the 0.001 electrons/ bohr^3 contour of the electronic density [Brinck, Murray and Politzer, 1992]. The general lack of correspondence between Π and the dipole moment μ can be seen by inspection of Table 3, as can also the general relationship between Π and the dielectric constant ϵ. For the nitro derivatives, a general trend is that Π increases as the carbon to NO_2 ratio decreases; the Π values for $C_6H_5NO_2$, p-$C_6H_5(NO_2)_2$ and CH_3NO_2 are 12.3, 16.5 and 19.9 kcal/mole, respectively. For the monosubstituted benzenes, the Π values range from 4.6 to 12.3 kcal/mole, with the largest value being that of nitrobenzene.

These observations and the known general trends in the impact/shock sensitivities of nitroaromatics led us to investigate the possibility that there might be a relationship between Π and impact sensitivity [Murray, Lane, Brinck and Politzer, 1992]. In Table 4 are listed experimentally-determined impact sensitivities and our earlier reported $V_{mid,max}$ values for a group of nitro-aromatics, along with their Π values and surface potential maxima. For these molecules, excluding the monohydroxy derivative (picric acid, 13), there is a linear correlation coefficient of 0.92 between impact drop height and $V_{mid,max}$. For the same group, the impact sensitivity and Π show a correlation coefficient of 0.98 [Murray, Lane, Brinck and Politzer, 1992].
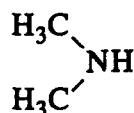
An interesting feature of the surface potentials of the nitroaromatics listed in Table 4 is that the most positive regions of electrostatic potential on the molecular surface are generally located above the C-NO_2 bonds and the center of the aromatic ring. (This can be seen in Fig. 3 for 1,3,5-

trinitrobenzene.) These positive regions are indicative of sites favorable for the initial approach of nucleophiles, and are consistent with the observed reactions of nitroaromatics with hydroxide and alkoxide ions to form Meisenheimer complexes [Gibson and Crampton, 1979; Crampton and Wilson, 1980; Bacaloglu, Bunton and Cerichelli, 1987], as well as their reactions with hydrogen halides [Nielsen, Chafin and Christian, 1984]. The monohydroxy derivative, **13**, stands out in that the positive surface potential associated with its hydroxyl hydrogen, about 58 kcal/mole, is fully 19 kcal/mole greater than that above its ring center, and is in fact much larger than the potential maxima normally found near alcohol and phenol hydrogens, which range from 25 to 49 kcal/mole [Murray and Politzer, 1992]. The highly positive nature of this hydrogen is consistent with our earlier study suggesting that nitronic acid formation through intramolecular proton transfer may contribute to the observed sensitizing effect of OH groups in nitroaromatics [Politzer, Seminario and Bolduc, 1989].

IV. Nitramines

Energetic secondary nitramines are an important class of explosives, as is seen from the fact that two of the most effective (yet highly sensitive) military explosives are nitramines: 1,3,5-trinitro-1,3,5-triazacyclohexane (**4**, RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (**7**, HMX). In this section we will begin with a discussion of structural and electronic properties that are unique to nitramines, followed by an overview of calculations of decomposition reactions of some specific nitramines and perspectives on the sensitivities of members of this class of explosives.

Organic amines and aza nitrogens are characterized by the presence of a "lone pair" of electrons which give rise to strongly negative regions in the molecular electrostatic potentials; however these are significantly weakened by the substitution of electron-withdrawing nitro groups on the amine nitrogens [Politzer and Murray, 1991]. As an extreme example, the negative potential in the lone pair region of dimethylamine (**28**) reaches a value of -100 kcal/mole (at the HF/STO-5G computational level) [Murray, Redfern, Seminario and Politzer, 1990], whereas in dimethylnitramine (**29**), there is <u>no</u> negative potential associated with the amine nitrogen [Murray, Redfern, Lane, Politzer and Willer, 1990].

$$
\begin{array}{cc}
\underset{\text{H}_3\text{C}}{\overset{\text{H}_3\text{C}}{\big\rangle}}\text{NH} & \underset{\text{H}_3\text{C}}{\overset{\text{H}_3\text{C}}{\big\rangle}}\text{N--NO}_2 \\
\mathbf{28} & \mathbf{29}
\end{array}
$$
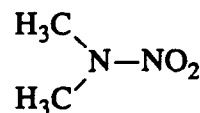
An interesting feature of aza nitrogens is an anomalous stabilization that is associated with their presence, and which we attribute to σ-conjugation of their lone pairs [Murray, Redfern, Seminario and Politzer, 1990]. We have identified this effect by means of the well-established

isodesmic reaction procedure [Hehre, Ditchfield, Radom and Pople, 1970; Hehre, Radom, Schleyer and Pople, 1986].

Secondary nitramines contain the subunit $R_1R_2N\text{-}NO_2$, the simplest example being dimethylnitramine, **29**; some others are shown below (**30** - **36**). In the course of several computational studies of nitramines [Politzer, Sukumar, Jayasuriya and Ranganathan, 1988; Murray, Sukumar, Ranganathan and Politzer, 1990; Murray, Redfern, Lane, Politzer and Willer, 1990; Habibollahzadeh, Murray, Redfern and Politzer, 1991], consistent trends have emerged. For
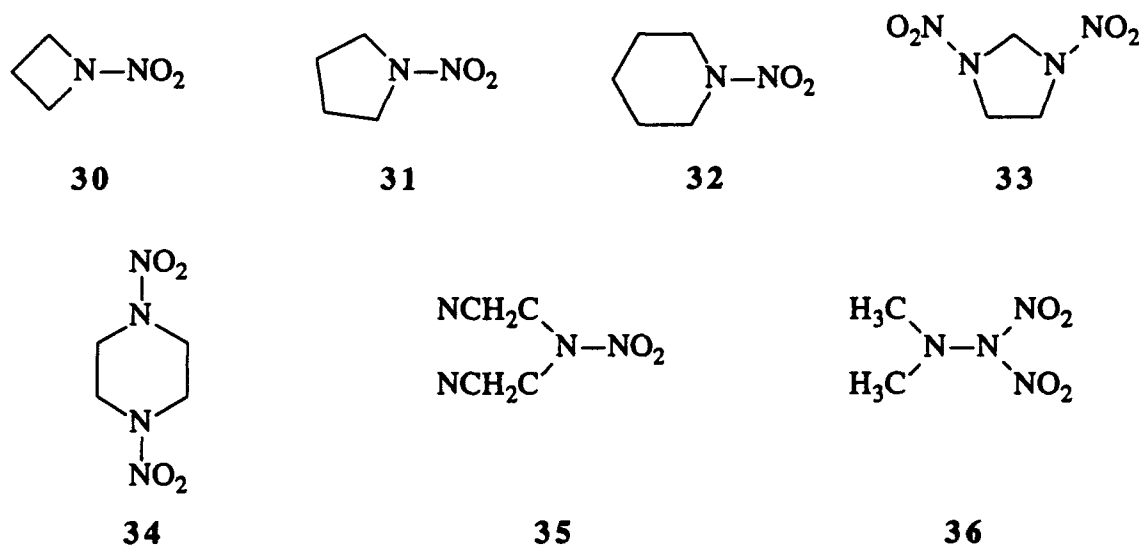
example, a decrease in the degree of pyramidal character of the amine nitrogen parallels a decrease in $N\text{-}NO_2$ bond length. This observation is consistent with greater delocalization of the amine lone pair into the bond with increasing planarity, as shown in eq. (13). For instance, the calculated HF/3-21G $N\text{-}NO_2$ bond lengths in 1,3-dinitroimidazolidine (**33**) are 0.04 Å shorter than those in

(13)
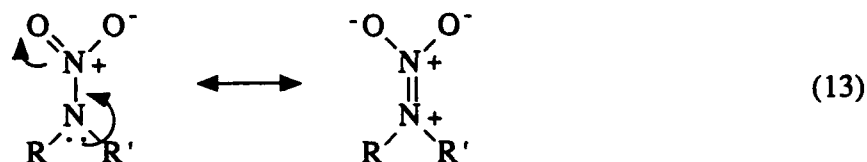
the less planar 1,4-dinitropiperazine (**34**) [Murray, Redfern, Lane, Politzer and Willer, 1990]. In accordance with these observations, we have shown that the $N\text{-}NO_2$ rotational barriers in nitramines are generally greater than $C\text{-}NO_2$ rotational barriers [Habibollahzadeh, Murray, Grice and Politzer, 1992], and that the former are largely dependent upon the degree of pyramidal character of the amine nitrogen in the ground state molecule [Habibollahzadeh, Murray, Redfern and Politzer, 1991].
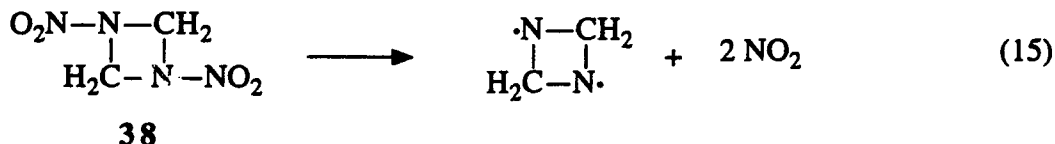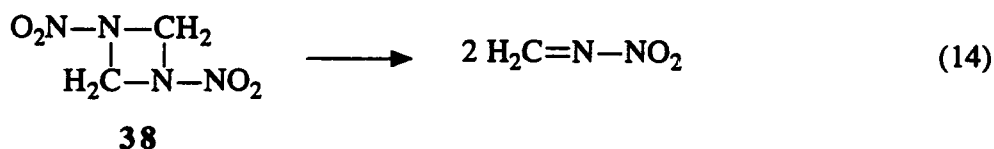
Due at least in part to their importance as energetic materials, there is a great deal of interest in the stabilities and the thermal decomposition mechanisms of nitramines. The overall consensus

is that rupture of the N-NO$_2$ bond is a key step in the process of decomposition, although there may be important competing pathways which may even predominate in some instances [Brill and Oyumi, 1986; Zhao, Hintsa and Lee, 1987; Stewart and Jeffries, Zellweger, McMillan and Golden, 1989; Saxon and Yoshimine, 1989; Grodzicki, Seminario and Politzer, 1990a; Grodzicki, Seminario and Politzer, 1990b; Habibollahzadeh, Grodzicki, Seminario and Politzer, 1991].

In several recent computational studies, we have focused upon some of the possible initial steps in the unimolecular thermal decompositions of 1,3-diazacyclobutane (37), 1,3-dinitro-diazacyclobutane (38), 1,3,5-triazacyclohexane (39) and its nitramine derivative RDX (4) [Grodzicki, Seminario and Politzer, 1990; Seminario, Grodzicki and Politzer, 1991; Grodzicki, Seminario and Politzer, 1991; Habibollahzadeh, Grodzicki, Seminario and Politzer, 1991]. In the
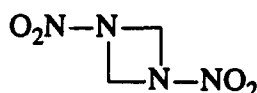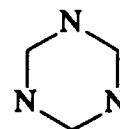
37   38   39

first of these, a vibrational analysis carried out at the *ab initio* HF/3-21G level pointed to two modes that clearly support bond rupture and molecular dissociation [Grodzicki, Seminario and Politzer, 1990]. One is a ring mode, while the other involves a stretching of the N-NO$_2$ bonds; the corresponding bond-breaking processes are shown in eqs. (14) and (15):

$$O_2N-N-CH_2 \atop H_2C-N-NO_2 \longrightarrow 2\ H_2C=N-NO_2 \qquad (14)$$

38

$$O_2N-N-CH_2 \atop H_2C-N-NO_2 \longrightarrow {\cdot N-CH_2 \atop H_2C-N\cdot} + 2\ NO_2 \qquad (15)$$

38

An important difference between the reactions depicted in eqs. (14) and (15) is that the former has an activation barrier while the latter, N-NO$_2$ bond scission, does not. The energetics analysis in this study led us to the conclusion that ring fragmentation is roughly competitive with N-NO$_2$ bond breaking as an initial step in the thermal decomposition of 38.

We have also investigated the nitro-nitrite rearrangement of 38, given in eq. (16), and have found it to be less likely than the processes shown in eqs. (14) and (15) [Grodzicki, Seminario and Politzer, 1990]. Rearrangements analogous to eq. (16) are believed to play important roles in the thermal decompositions of dimethylnitramine, 29 [Stewart, Jeffries, Zellweger, McMillen and

Golden, 1989] and nitramide (H_2NNO_2) [Saxon and Yoshimine, 1989; Seminario and Politzer, 1992].

$$(16)$$

38
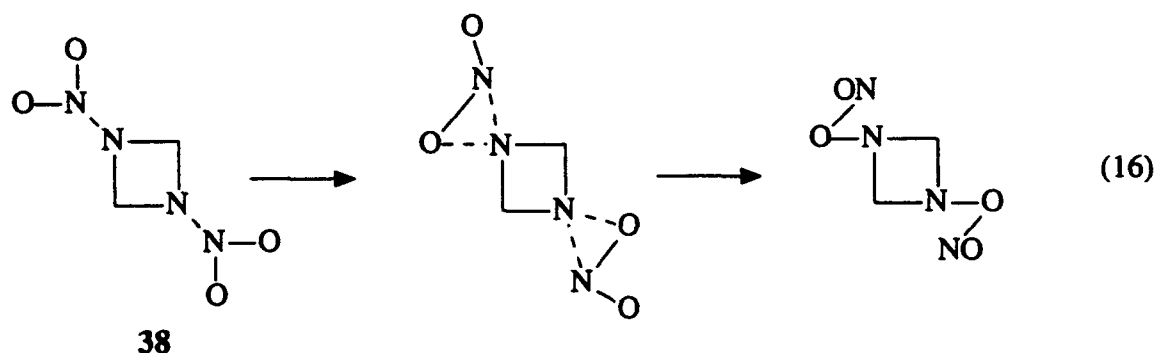
The pathway depicted in eq. (14) is analogous to the concerted symmetric ring opening that has been proposed as the "dominant primary channel" in the thermal decomposition of RDX, **4** [Zhao, Hintsa and Lee, 1987]. We have recently investigated, using *ab initio* and local density functional (LDF) methods, the activation barriers to the concerted gas-phase ring fragmentations of 1,3,5-triazacyclohexane (**39**) and its trinitro derivative **4**, shown in eqs. (17) and (18) [Habibollahzadeh, Grodzicki, Seminario and Politzer, 1991]. We found that the calculated barriers

$$3\ H_2C{=}NH \qquad (17)$$

39

$$3\ H_2C{=}N{-}NO_2 \qquad (18)$$

4
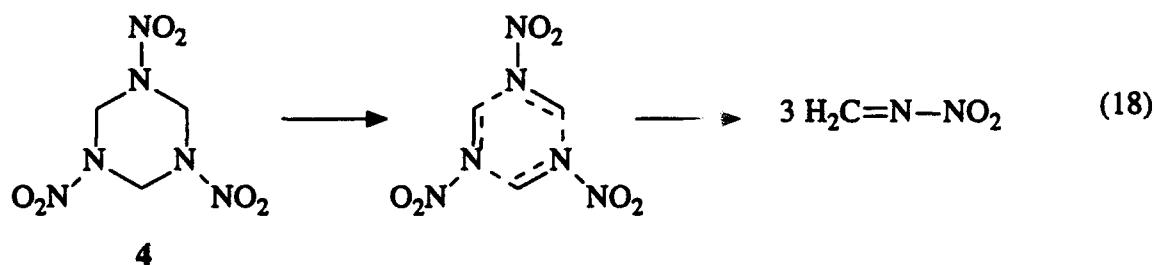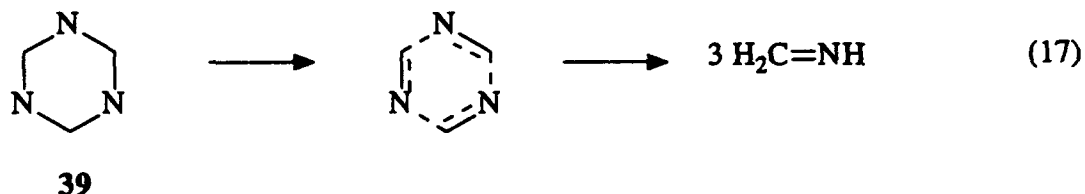
decrease as the *ab initio* computational level increases, with the LDF values being somewhat smaller in magnitude than the best Hartree-Fock or post-HF. This conclusion was also reached in a comparison of *ab initio* and LDF activation energies for the process shown in eq. (14) [Grodzicki, Seminario and Politzer, 1991], as well as for some small molecule isomerizations [Seminario, Grodzicki and Politzer, 1990]. Our predicted activation energies for eqs. (17) and (18) are in the range 72 - 75 kcal/mole. These results are consistent with the experimental findings by Zhao *et al* [1987] in molecular beam work that the activation energy for the reaction given in eq. (18) is not more than 80 kcal/mole.

Understanding factors affecting the sensitivities of nitramines has been a key emphasis in energetic materials research. As we have mentioned, considerable attention has focused upon cleavage of the $N-NO_2$ bond as a key step in the process of decomposition, initiated by heat, shock or impact. We have recently demonstrated [Politzer, Murray, Lane, Sjoberg and Adolph, 1991] that a good correlation can be obtained between the shock sensitivities of the nitramines 4, 7, 33 - 35, 40 and 41 and molecular properties, by (a) explicitly taking each $N-NO_2$ bond into account,
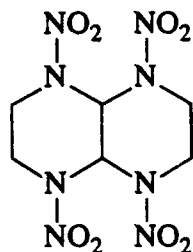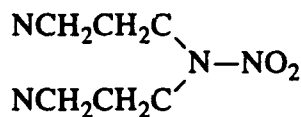
40   41

and (b) recognizing that its effectiveness in triggering decomposition is "diluted" as the molecule becomes larger. A straightforward formulation of these ideas is,

$$\text{Sensitivity} \sim \frac{1}{M}\sum_{i=1}^{n}\frac{1}{R_i^{-1}} = \frac{1}{M}\sum_{i=1}^{n}R_i = \frac{n}{M}R_{ave} \tag{19}$$

in which n is the number of $N-NO_2$ linkages in the molecule, having N-N distances R_i, and M is the molecular weight. M is taken as a measure of molecular size, and the reciprocal of R_i as our measure of bond strength. For the molecules listed above, a linear relationship exists between (n/M) R_{ave} and shock sensitivity, with a correlation coefficient of 0.94. (For a group of five nitroaliphatics, a similar relationship was found, where n is the number of $C-NO_2$ linkages and R_i is the C-N bond length.)

It should be mentioned that for this group of nitramines, shock sensitivity also correlates well with n/M alone; indeed the latter has been investigated as an indicator of impact sensitivity [Adolph, Holden and Cichra, 1980]. However the extensive experimental evidence pointing to $N-NO_2$ scission as a key step in nitramine decomposition argues that the strengths of these bonds should be explicitly reflected in any measure of sensitivity.

Another, yet consistent formulation of these concepts is our measure of local polarity, Π [Brinck, Murray and Politzer, 1992] . Analogously to the $C-NO_2$ systems in Tables 3 and 4, Π increases as the ratio of $N-NO_2$ groups to carbon atoms in the framework increases, and so does sensitivity to shock. Our calculated Π values for 1,4-dinitropiperazine (34), 1,3-dinitroimida- zolidine (33) and RDX (4) are 17.1, 18.5 and 19.4, respectively, which show a correlation coefficient of 1.00 with shock sensitivity [Murray, Lane, Brinck and Politzer, 1992].

V. Strained Cagelike Molecules

Strained molecules have been a topic of both fundamental and applied interest in chemistry for more than a century [Baeyer, 1885; Greenberg and Liebman, 1978]. The Commission on Physical Organic Chemistry defines the term strain as follows: "Strain is present in a molecular entity or transition structure if its energy is increased because of unfavorable bond lengths, bond angles, or dihedral angles relative to a standard." [Doyle, 1992] In the area of energetic materials research, strained frameworks are useful starting points in designing new systems because of their higher energy content, which is subsequently released upon decomposition.

Three-, four- and five-membered rings (42 - 44) fused together in a cagelike fashion are often classified as strained "cagelike" molecules. Among hydrocarbons, some examples are

42   43   44
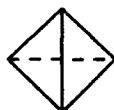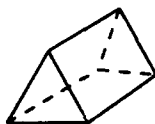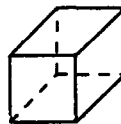
45   46   47   48

tetrahedrane (45), triprismane (46), cubane (47) and homocubane (48). A key characteristic of 42, 43 and 45 - 48 is the small endocyclic bond angles imposed by the three- and four-membered rings; for tetracoordinate carbon, normal bond angles are in the neighborhood of $109°$. This bond angle distortion is a destabilizing factor contributing to the overall strain inherent in these systems [Greenberg and Liebman, 1978].

We have earlier developed an index which provides an effective means for characterizing individual strained bonds [Politzer, Abrahmsen, Sjoberg and Laurence, 1983]; it is based on the "bond path" concept [Bader, Tang, Tal and Biegler-König, 1982a and 1982b]. A bond path is the path between two bonded nuclei that goes through the saddle point in the internuclear electronic density and follows the maximum density gradient to each nucleus; it can be visualized as the ridge of highest electronic density linking the two nuclei. For many bonds, such as those between the carbons in propane and cyclohexane, the bond path is essentially identical with the internuclear axis; in other cases, such as molecules with inherent bond angle strain, there can be a significant difference between the two [Politzer, Abrahmsen, Sjoberg, and Laurence, 1983; Politzer, Bar-Adon and Miller, 1987; Politzer, Jayasuriya and Zilles, 1985; Politzer, Kirschenheuter and Alster,

1987; Politzer and Murray, 1988; Politzer and Seminario, 1989]. Our "bond deviation index" was introduced as a numerical measure of the degree to which a given bond path differs from a defined reference path; it can be viewed as reflecting bond angle strain. A thorough discussion of this index is given elsewhere [Politzer and Murray, 1988].

In Table 5 are listed our bond deviation indices for a variety of strained hydrocarbons. It can be seen that the C-C bonds of three-membered rings have the highest values, even when the latter is fused to a larger ring. Also included in Table 5 are calculated isodesmic reaction energies (computed at the HF/3-21G level) for some of the molecules; these values can be interpreted as reflecting relative degrees of overall molecular strain. The $\Delta E_{isodesmic}$ values of the cagelike frameworks **45 - 47** are considerably greater in magnitude than their respective building blocks cyclopropane and cyclobutane (as might be anticipated). However the individual bonds within **45 - 47** can be characterized as either "cyclopropane-like" or "cyclobutane-like" by inspection of their bond deviation indices.

Despite the difference in the bond angle strain associated with three- and four- membered rings, as is reflected in their bond deviation indices, cyclopropane and cyclobutane are reported to have very similar strain energies [Greenberg and Liebman, 1978]. The low, seemingly anomalous strain energy of the former is attributed to the stabilizing effect of "σ-aromaticity" [Dewar, 1979]. This is important to keep in mind in designing potential energetic systems. Cyclopropane itself does not contain a significant amount of strain energy; however modifications of this ring that disrupt the σ-aromaticity, such as unsaturation or the formation of cagelike systems, can result in a high strain energy.

Another interesting feature of strained hydrocarbons is that regions of negative electrostatic potential are associated with their C-C bonds [Politzer, Domelsmith, Sjoberg and Alster, 1982; Politzer, Domelsmith and Abrahmsen, 1984; Politzer and Murray, 1988]. (This is not observed for the C-C bonds of unstrained hydrocarbons.) The most negative potentials are near the bond midpoints, and their presence indicates that these bonds themselves can serve as initial sites for electrophilic attack. The olefin-like properties of cyclopropane [Cromwell and Graff, 1952] and bicyclobutane [Wiberg, 1965] and the tendency of the former for edge hydrogen bonding [Legon, Aldrich and Flygare, 1982] can be interpreted as reflecting this feature, as can the observed cation-catalyzed rearrangements of cubane and homocubane [Cassar, Eaton and Halpern, 1970; Paquette, Boggs and Ward, 1975], in which the inital step is an interaction between the positive ion and a C-C bond.

It is perhaps tempting to view the existence of bent bonds in strained molecules as the reason for the negative bond potentials. However we have found that the substitution of electron-withdrawing groups, such as NO_2 and Cl, eliminates the negative C-C bond potentials in strained hydrocarbons but does not significantly affect the degrees of curvature of the bond paths (or their bond deviation indices) [Politzer and Murray, 1988]. On the other hand, density difference plots

do show that electronic charge has been depleted in the internuclear regions of these derivatives. Thus, two key points that have emerged from these findings are that (a) bent bonds do not necessarily produce negative bond potentials, and (b) the degree of bending in a strained bond is not directly related to the quantity of electronic charge in the bond region.

We have also shown that the introduction of oxygen or nitrogen into strained rings diminishes the bond deviation index of the C-X bond (where X is O or N) relative to the parent hydrocarbon [Politzer, Abrahmsen, Sjoberg and Laurence, 1983; Politzer, Bar-Adon and Miller, 1987; Politzer and Seminario, 1989], suggesting a slight decrease in bond angle strain. In addition, endocyclic nitrogens or oxygens effectively eliminate any negative potentials associated with C-C bonds; instead characteristic strongly negative regions are associated with the nitrogens and oxygens, indicating these to be favorable sites for electrophilic attack [Politzer and Murray, 1991]. The slightly stabilizing effect of the introduction of oxygen or nitrogen in strained ring systems is also reflected in the molecule as a whole, as can be seen from calculated isodesmic reaction energies [Alkorta, Elguero, Rozas and Balaban, 1990; Murray, Seminario, Lane and Politzer, 1990; Politzer and Murray, 1992]; for example, the calculated HF/3-21G $\Delta E_{isodesmic}$ of azacubane is 121 kcal/mole, compared to 127 kcal/mole for cubane (**47**). Thus the presence of aza nitrogens in cagelike systems has been suggested as being desirable [Murray, Seminario and Politzer, 1991], in that they may mitigate excessive strain. For although strain is viewed as advantageous for energetic systems, a high degree of it can lead to practical problems in the synthesis and isolation of a proposed compound.

In the past decade, a variety of strained cagelike compounds have been proposed as target energetic molecules. These have included, for example, nitro derivatives of cubane and other cage-like frameworks. To further the synthesis of such compounds, we have investigated computation-ally the bond-weakening tendency associated with NO_2 and NH_2 being bonded to adjacent tertiary carbons in strained cagelike hydrocarbons, which has hampered efforts to synthesize 1,2-dinitro-cubane from 1-amino-2-nitrocubane [Griffin and Marchand, 1989; Marchand, 1989].

When NO_2 and NH_2 are substituents on adjacent tertiary carbons in some strained molecules, e.g. 1-nitro-3-aminobicyclobutane (**49**) and 1-amino-2-nitrocubane (**50**), there is a marked weakness of the intervening C-C bond (i.e. C_1-C_3 in **49** and C_1-C_2 in **40**), as measured
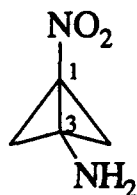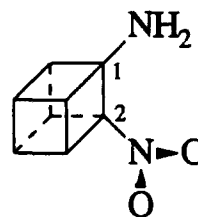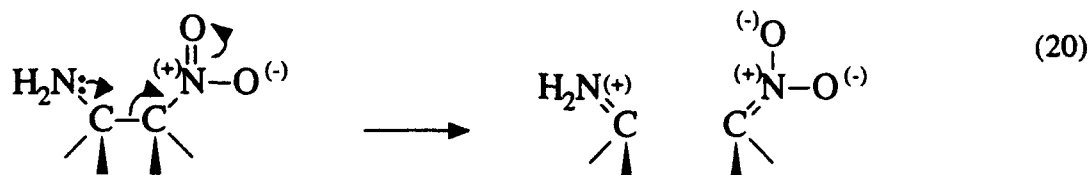

49   **50**

by means of the calculated bond order [Politzer, Kirschenheuter and Alster, 1987; Murray, Seminario and Politzer, 1991]. This phenomenon is well known to organic chemists and has been attributed to a "push-pull" mechanism, which in the limiting case would lead to a rupture of the C-C bond, as illustrated in eq. (20):

$$(20)$$

As an extreme example of this, we have found that the conformer of aminonitrotetrahedrane in which the O-N-O and N-C_1-C_2 planes are initially set to be perpendicular (51) does not optimize to a local energy minimum but rather rearranges preferentially to 1-amino-3-nitrocyclobutadiene (52), as shown in eq. (21) [Grodzicki, Seminario and Politzer, 1990].

$$(21)$$

51   52
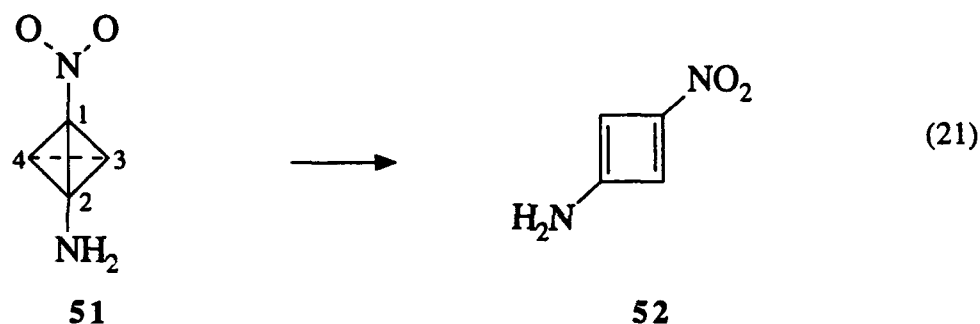
In more recent computational analyses, we have found that the push-pull mechanism depicted by eq. (20) is actually the consequence of two separate effects, associated with the NH_2 and NO_2 groups individually, which can in some instances reinforce each other [Murray, Seminario and Politzer, 1991a, 1991b; Murray, Concha, Seminario and Politzer, 1991]. In studies of various aminocubanes, aminoazacubanes, aminotriprismanes and aminoazatriprismanes, we found a consistent direction-specific bond weakening in one (and only one) of the C-C or C-N bonds adjacent to the site of NH_2 substitution. The weakened C-X bond (where X=C or N) is invariably coplanar with the C-NH_2 bond and the position of the most negative electrostatic potential (V_{min}) associated with the amine nitrogen lone pair. This tendency for a co-planar alignment of the lone pair and a C-X bond is a manifestation of the anomeric effect [Dewar, 1984] and reflects the possibility of the delocalization of the lone pair as shown in eq. (22):

$$(22)$$
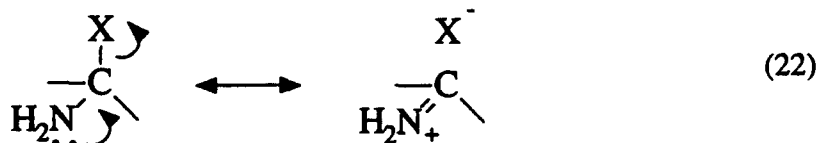
This delocalization, which weakens the C-X bond, can occur most effectively when the latter is coplanar with the lone pair. We have found that this effect is stronger when X=N (rather than X=C), consistent with the anomeric effect being most commonly invoked for molecules in which X is an electronegative atom, e.g. N,O or F.

The situation involving the NO_2 group alone is less straightforward than that of the NH_2, because it can strengthen some bonds and weaken others, depending upon its conformation [Grodzicki, Seminario and Politzer, 1990; Murray, Seminario and Politzer, 1991a; Murrray, Concha, Seminario and Politzer, 1991]. For example, in studying nitrotetrahedrane (53) and nitrocubane (54) we found that when the O-N-O plane is perpendicular to an N-C-C plane, then
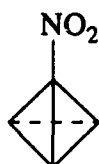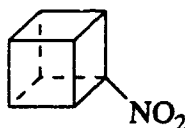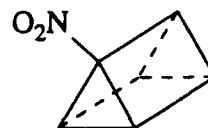
53   **54**   **55**

that C-C bond is weakened slightly; however C-C bonds that are coplanar (or nearly so) are slightly strengthened. It was shown through an orbital correlaticn analysis of **53** that the weakening can be attributed to an interaction between a π-type NO_2 orbital and the C-C bonding orbital [Grodzicki, Seminario and Politzer, 1990].

Our results for nitrotriprismane, **55**, do not follow the same pattern as was found in **53** and **54** [Murray, Concha, Seminario and Politzer, 1991]. In nitrotriprismane we found computationally that only one orientation of the NO_2 corresponds to a local energy minimum; this is when the NO_2 group is coplanar with the C-C bond joining the three-membered rings. This is accompanied by a weakening of the adjacent three-membered-ring C-C bonds. This was rationalized by analysis of the electronic structure of triprismane.

Thus vicinal NH_2, NO_2 groups will weaken the C-C bond joining them when both the NH_2 and NO_2 bond-weakening tendencies affect this particular bond and reinforce each other, e.g. in **49** and **50**; this can be described by the push-pull mechanism depicted in eq. (20). However neighboring NO_2 and NH_2 groups may also act upon different bonds, e.g. in the cases of **56** and **57**; in these, the NO_2 weakens the adjacent C-C bonds in the three-membered ring, while the NH_2 acts on the bond in the four-membered ring [Murray, Concha, Seminario and Politzer, 1991].
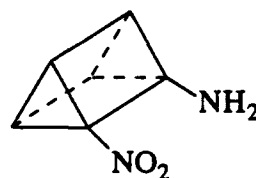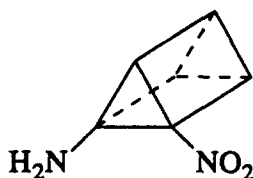
56   57

In the course of our studies of nitro derivatives of aza cagelike systems, a finding of interest for the design of new energetic materials has emerged. This is the observation that the C-C bond weakening that we have found to be associated with NO_2 in these systems does not occur to any significant degree when there is an adjacent aza nitrogen [Murray, Seminario and Politzer, 1991a; Murray, Concha, Seminario and Politzer, 1991]. Taken in conjunction with the overall stabilizing influence of aza nitrogens (through diminishing the molecular strain energy) [Murray, Seminario, Lane and Politzer, 1990], this further emphasizes the advantages of aza nitrogens from
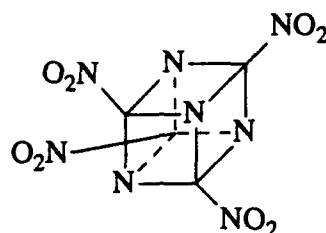
58

the standpoints of synthesis and stability. Thus, we have suggested that target systems such as the tetranitrotetraazacubane 58 are plausible from a synthetic standpoint and should be further investigated as potential high-energy molecules [Murray, Seminario and Politzer, 1991a]. (58 could in principle be made from amine precursors, with no possibility of vicinal NH_2,NO_2 combinations.) This suggestion is generally consistent with comments made by Engelke and Stine in an *ab initio* SCF-MO study of octaazacubane (N_8) [Engelke and Stine,1990]; they stated that "the known high stability of $(CH)_8$ and the predicted high energy of N_8 cubane suggest that there are probably intermediate mixed carbon-nitrogen cubane-like structures that would be stable high-energy materials." This comment was applied also to nitrated azacubanes.

VI. High-Nitrogen-Content Molecules

There is a growing interest in high-nitrogen-content molecules as potential energetic materials [Benson, 1984], prompting a variety of theoretical studies [e.g. Mayers, Salter, Bartlett, Salter, Hess and Schaad, 1988; Engelke, 1989, 1990; Engelke and Stine, 1990; Politzer and Seminario, 1990; Thomas, Quelch and Schaefer, 1991; Seminario, Concha and Politzer, 1992; Politzer, Murray, Seminario and Miller, 1992]. In this section we will discuss calculations that have been carried out for molecules in this category which contain three or more linked nitrogens (nitrogen catenation).

Nitrogen catenation is often associated with instability and/or sensitivity [Benson, 1984]. For example, the powerful explosive 1,3,5-triazido-2,4,6-trinitrobenzene (59) undergoes a slow conversion to hexanitrosobenzene (60) and N_2 [eq. (23)],

$$59 \longrightarrow 60 + 3\ N_2 \qquad (23)$$
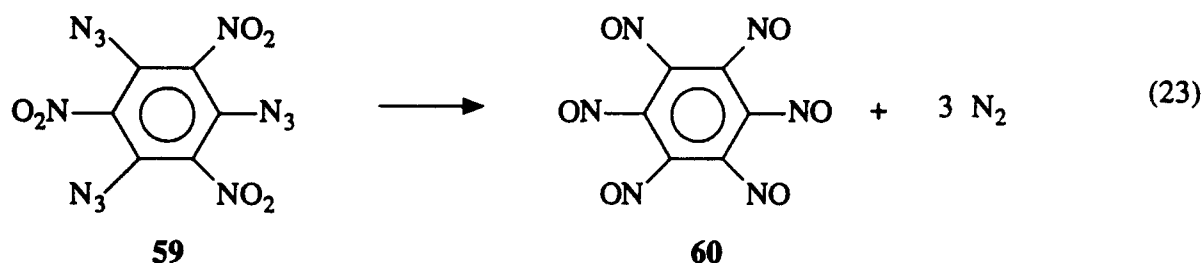
eventually losing its initiating power [Meyer, 1987]. On the other hand, the tetrazene **61** has been found to be quite insensitive to impact [Benson, 1984] and the tetraazapentalene **62** is known to have a high level of thermal stability [Meyer, 1987]. These findings raise the question of what

$$(H_3C)_2N-N=N-N^{\pm}=CH-C \overset{NO_2^-}{\underset{NO_2}{\diagdown}}$$

6 1

6 2
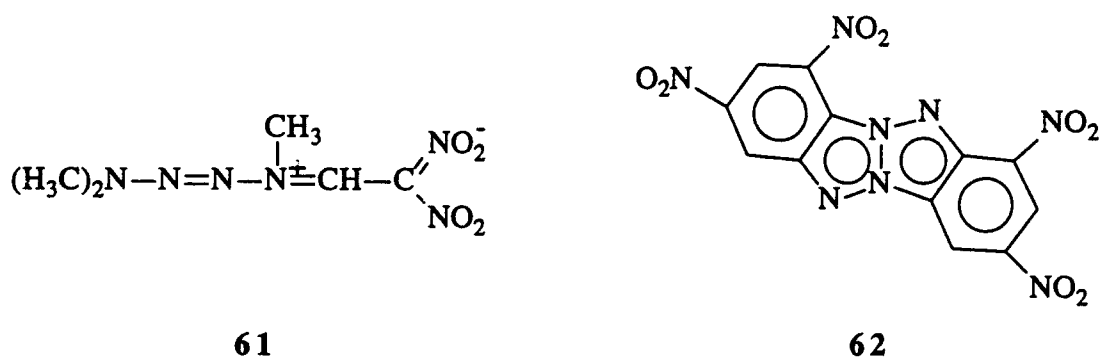
factors are important in determining the stabilities of molecules with nitrogen catenation. Several studies addressing this point will be discussed.

In an earlier computational analysis of some tetraazapentalenes [Politzer and Seminario, 1990], we found that the parent molecule **63** is significantly more stable than the isomer **64**. Our

6 3

6 4

computed structure for **63** showed that there is considerable delocalization of charge, as can be depicted by resonance structures **63a** - **63e**. In contrast, **64** has localized N=N and C=C double

63a   **63b**   **63c**   **63d**   **63e**
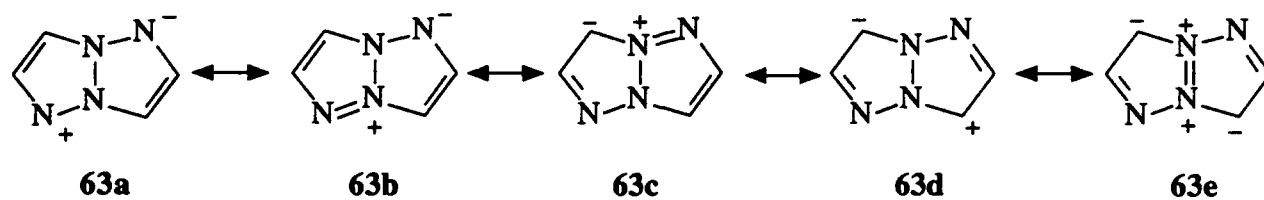
bonds. The former may be a destabilizing feature, since it may promote decomposition through elimination of N_2.
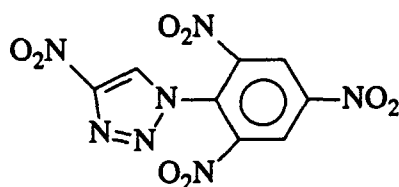
The importance of this factor is brought out very strikingly by the pairs of isomeric triazoles **65, 66** and **67, 68**; their measured sensitivities, given as impact drop heights, are shown in parentheses [Storm, Ryan, Ritchie, Hall and Bachrach, 1989]. **65** and **67** are clearly more
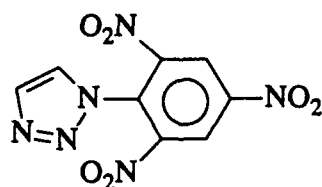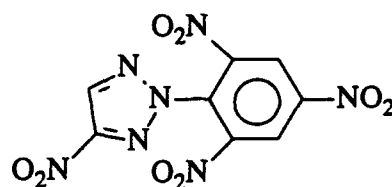

65 (11 cm)
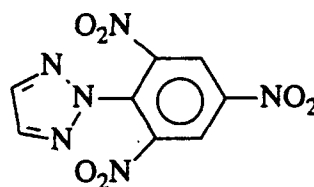
66 (200 cm)

67 (9 cm)

**68** (67 cm)

sensitive to impact than their isomers **66** and **68**. The crystallographically-determined structures of **65 - 68** show that the primary structural difference within each pair of isomers is that the N_b-N_c bonds in the triazole rings of **65** and **67** are about 0.03 Å shorter than the other N-N bonds. (In **65** and **67**, N_a is the nitrogen linked to the phenyl portion.) It was suggested that this facilitates the decomposition of **65** and **67** through the loss of N_2, accounting for the greater sensitivities of these two isomers [Storm, Ryan, Ritchie, Hall and Bachrach, 1989].

The evidence presented suggests that nitrogen catenation may be compatible with stable systems provided that there is considerable conjugation between the nitrogens; one indication of this is similarity of the N-N bond lengths. The presence of some shorter, stronger N-N bonds is a warning of possible instability/sensitivity due to facile decomposition through N_2 elimination. (An extreme example is provided by the azides, R-N=N=N, many of which are highly explosive, and decompose through release of N_2; the outer N-N bond lengths are typically about 1.12 Å [Allen, Kennard, Watson, Brammer, Orpen and Taylor, 1987], nearly the same as free N_2, 1.098 Å.) This structural criterion can also be applied to a recent computational study of the unknown unsubstituted tetrazines **69** and **70** [Thomas, Quelch and Schaefer, 1991]. In **69**, the *ab initio* CISD/DZP computed N-N bond lengths are 1.330, 1.297 and 1.330 Å; in **70** they are both
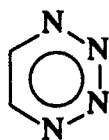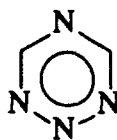
69   **70**   **71**

1.311 Å. **70** is found to be the more stable of the two isomers. The only known tetrazine is **71**, in which the CISD/DZP N-N distances are 1.310 Å.

In the case of hypothetical molecules that have not yet been observed or isolated, a key question is whether they can exist even in principle. This can be addressed computationally by carrying out a vibrational frequency analysis for the structure of interest; if this yields no imaginary frequencies, then the structure corresponds to a local minimum on the energy surface [Hehre, Radom, Schleyer and Pople, 1986]. For example, the unknown tetrazines **69** and **70** have both been shown computationally to be local minima on the $C_2N_4H_2$ energy surface [Thomas, Quelch and Schaefer, 1991]. The same is true of pentazine (**72**) [Politzer, Murray, Seminario and Miller, 1992], and the N_6 analogue of benzene (**73**), along with four of its cyclic isomers **74 - 77** [Engelke, 1989], none of which have as yet been confirmed experimentally. In the case of **72**, the computational analysis was at the post-Hartree-Fock MP2/6-31G* level, but for **73 - 77**, the conclusions were drawn from HF/4-31G* calculations. **73** is predicted to be the most stable of the
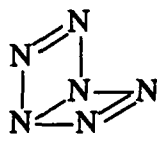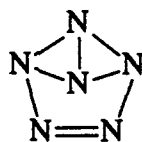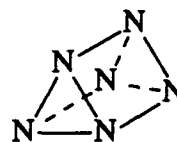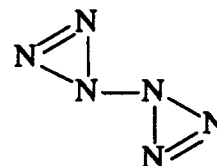

**72**   **73**   **74**   **75**   **76**   **77**

cyclic N_6 isomers [Engelke, 1989], which is consistent with its having six equivalent N-N bonds and aromatic character; **74, 75** and **77** each have one or two localized N-N double bonds, while hexaazatriprismane (**76**) has two types of N-N single bonds.

It has been demonstrated by us [Seminario, Concha and Politzer, 1991] and by others [Clabo and Schaefer, 1987; Coffin and Pulay, 1991] that reliable assessment of the structures and stabilities of molecules containing a large proportion of strongly electronegative atoms (N, O, F, etc.) requires that electronic correlation be taken into account, especially if these atoms are linked, as in H_2O_2 [Politzer and Murray, 1992]. For example, in a study of furoxan (**78**: 1,2,5-oxadiazole-2-oxide) and some of its isomers (e.g. **79 - 82**), we showed that the structural data and predicted stabilities were markedly dependent upon the computational method and level used for the geometry optimizations. For instance, MP2/6-31G* calculations revealed **81** and **82** to be unstable, although HF/3-21G and HF/6-31G* had shown local minima.

$$78 \qquad 79 \qquad 80 \qquad 81 \qquad 82$$
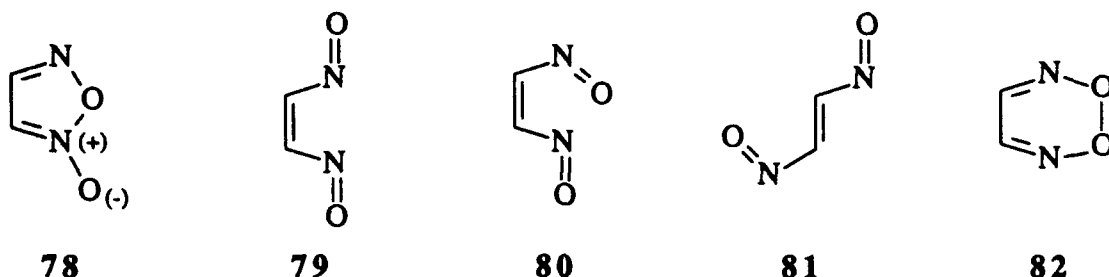
Pentazine, **72**, is predicted to be a stable system at both the HF/3-21G and MP2/6-31G* levels; the computed geometries are very similar, with the C-N and N-N bond distances differing by 0.014 and less than 0.009Å, respectively [Politzer, Murray, Seminario and Miller, 1992]. On the other hand, the N-N bond lengths calculated by post-Hartree-Fock methods for triaziridine (**83**) are 0.054 Å longer than those obtained at the HF/6-31G* level [Magers, Salter, Bartlett, Salter, Hess and Schaad, 1988]. It may be that Hartree-Fock methods are reliable for aromatic aza systems, e.g. pyridine, the tetrazines, pentazine and N_6 benzene, but they certainly should be applied with caution to high-nitrogen systems in general.

83
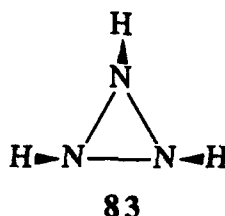
## VII. Overview of Structure-Sensitivity Relationships

Our shock sensitivity relationships for nitramines and nitroaliphatics suggest that the strengths and numbers of X-NO$_2$ linkages in relation to overall molecular size are important in determining sensitivity [Politzer, Murray, Lane, Sjoberg and Adolph, 1991]. Our observation, for a few nitramines, that sensitivity varies directly with local polarity (as measured by Π) is consistent with this relationship [Murray, Lane, Brinck and Politzer, 1992]. It is intuitively reasonable to anticipate that local polarity should increase as the number of X-NO$_2$ linkages per unit volume increases.

In the area of nitroaromatics, correlations between impact/shock sensitivity and total electron-donating ability of the non-nitro substituents [Owens, 1984], or V_{mid} or $V_{mid,max}$ [Owens, Jayasuriya, Abrahmsen and Politzer, 1985; Murray, Lane, Politzer and Bolduc, 1990] suggest that the strengthening of C-NO$_2$ linkages leads to decreased sensitivity. A direct relationship between nitroaromatic impact sensitivity and local polarity [Murray, Lane and Politzer, 1992], is again not inconsistent with this viewpoint, in that Π decreases in response to the addition of electron-donating groups and increases with the addition of electron-withdrawing groups. The

implications of correlations between local polarity and impact/shock sensitivity are being further investigated.

Molecules which do not fit the general types of relationships that have been found to exist between impact/shock sensitivity and molecular and/or structural properties suggest starting points for further investigations aimed at understanding critical molecular features which may be determinants of sensitivity in certain specific cases. For example, we have suggested that the anomalously high sensitivities of hydroxyaromatics may be due to formation of small quantities of unstable nitronic acid tautomers [Politzer, Seminario and Bolduc, 1989]. Table 4 shows that the surface electrostatic potential of the OH hydrogen in the monohydroxy derivative picric acid 13 is considerably more positive than the areas above and below the aromatic ring. This is unusual for trinitroaromatics, and supports our earlier speculation that the facile loss of a phenolic hydrogen may in part account for the high sensitivities of hydroxynitroaromatics.

The 1-picryl-1,2,3-triazoles 65 and 67 are another example of anomalously high sensitivity being attributed to a molecular feature other than X-NO_2 linkages, in particular the presence of a relatively short N-N bond which may favor the facile elimination of N_2 [Storm, Ryan, Ritchie, Hall and Bachrach, 1989]. This may also be an important factor in determining the sensitivities of the isomers 4-nitro-1,2,3-triazole (84) and 3-nitro-1,2,4-triazole (85); the impact drop heights of these are 25 and >320 cm, respectively. We have found that the former, more

84   85
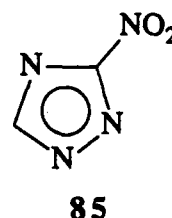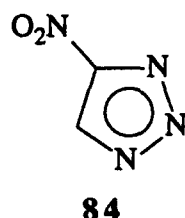
impact sensitive compound has calculated HF/3-21G N-N bond lengths of 1.287 and 1.398 Å, respectively, while the N-N distance in 85 is 1.420 Å. The relatively short N-N bond length in 84 is suggestive of a localized double bond, favoring the elimination of N_2.

In general nitramines are more sensitive to impact/shock than are nitroaromatics; e.g. see Table 1. In this context it may be relevant to point out that the experimentally-determined C-NO_2 rotational energy barriers for nitromethane, nitrobenzene and nitroethylene range from 0 - 5 kcal/mole (increasing in that order) [Høg, Nygaard and Sorensen, 1971; Meyer, Gammeter, Smith, Kühne, Nösberger and Günthard, 1973; Correl, Larson and Pedersen, 1980], while that of the N-NO_2 bond in dimethylnitramine is greater than 9 kcal/mole [Kintzinger, Lehn and Williams, 1969], as are also the theoretically predicted N-NO_2 rotational barriers of a series of alicyclic nitramines [Habibollahzadeh, Murray, Redfern and Politzer, 1991; Habibollahzadeh, Murray, Grice and Politzer, 1992]. It was proposed by Kamlet and Adolph [1981] that X-NO_2 rotation provides a means for dissipating thermal energy that otherwise might be used to initiate

decomposition. Thus it can be speculated that the lower rotational energy barriers of $C-NO_2$ bonds in nitroaromatics relative to the $N-NO_2$ in nitramines may contribute to the generally higher sensitivities of the latter. The higher barrier to rotation of the $N-NO_2$ linkage may impede the dissipation of thermal energy and lead to generally greater sensitivity.

Our discussion of sensitivity and its relationship to molecular properties has focused upon general correlations that exist within separate classes of compounds, e.g. nitroaromatics, nitramines and nitroaliphatics, and upon exceptions to these relationships which suggest alternative mechanisms to $X-NO_2$ bond cleavage as being operative in specific instances. Thus, although we believe it to be unlikely that an unequivocal universal relationship between sensitivity and molecular parameters can be established, considerable progress has indeed been made in understanding factors that influence sensitivity within separate classes of energetic systems as well as in certain exceptional cases. In the area of high-nitrogen-content molecules, it appears that reliable structural analyses are particularly important in assessing stability and/or sensitivity; in a number of cases, the presence of localized N-N bonds appears to be a factor favoring instability/high sensitivity.

References

Adolph, H. G., Holden, J. R. and Cichra, D. A. (1981) Technical report 80-495, Naval Surface Weapons Center.

Alkorta, I., Elguero, J., Rozas, I. and Balaban, A. T. (1990) "Theoretical Studies of Aza Analogues of Platonic Hydrocarbons. Part 1. Cubane and Its Derivatives" J. Mol. Struct. (Theochem) 206, 67.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. and Taylor, R. (1987) "Tables of Bond Lengths determined by X-Ray and Neutron Diffraction. Part 1. Bond Lengths in Organic Compounds" J. Chem. Soc. Perkin II, S1.

Allinger, N. L., Cava, M. P., DeJongh, D. C., Johnson, C. R., Lebel, N. A. and Stevens, C. L. (1971) Organic Chemistry, Worth Publishers, New York, chap. 16.

Alster, J., Slagg, N., Dewar, M. J. S., Ritchie, J. P. and Wells, C. (1981) "A Reaction Mechanism in the Shock Inititation of Detonation. A Theoretical Study." Fast Reactions in Energetic Systems, C. Capellos and R. F. Walker, eds., D. Reidel Pub. Co., Dordrecht, The Netherlands, 695.

Bader, R. F. W., Tang, T. -H., Tal, Y. and Biegler-König, F. W. (1982) "Molecular Structure and Its Change: Hydrocarbons" J. Am. Chem. Soc. 104, 940.

Bader, R. F. W., Tang, T. -H., Tal, Y. and Biegler-König, F. W. (1982) "Properties of Atoms and Bonds in Hydrocarbon Molecules" J. Am. Chem. Soc. 104, 946.

Bader, R. F. W., Carroll, M. T., Cheeseman, J. R. and Chang, C. (1987) "Properties of Atoms in Molecules: Atomic Volumes" J. Am. Chem. Soc. 109, 7986.

Bacaloglu, R., Bunton, C. A. and Cerichelli, G. J. (1987) "Intermediates in Nucleophilic Aromatic Substitution" J. Am. Chem. Soc. 109, 621.

Baeyer, A. (1885) "Ueber Polyacetylenverbindungen" Chem. Ber. 18, 2269.

Benson, F. R. (1984) The High Nitrogen Compounds, Wiley-Interscience, New York.

Brinck, T., Murray, J. S. and Politzer, P. (1991) "Relationships Between the Aqueous Acidities of Some Carbon, Oxygen and Nitrogen Acids and the Calculated Surface Local Ionization Energies of Their Conjugate Bases." J. Org. Chem., 56, 5012.

Brinck, T., Murray, J. S, Politzer, P. and Carter, R. E. (1991) "A Relationship Between Experimentally-Determined pKa's and Molecular Surface Ionization Energies for Some Azines and Azoles." J. Org. Chem., 56, 2934.

Brinck, T., Murray, J. S. and Politzer, P. (1992) "Quantitative Determination of the Total Local Polarity (Charge Separation) in Molecules" Molecular Physics, in press.

Brill, T. B. and Oyumi, Y. J. (1986) "Thermal Decomposition of Energetic Materials. 9. A Relationship of Molecular Structure and Vibrations to Decomposition: Polynitro-3,3,7,7-tetrakis (trifluoromethyl)-2,4,6,8-tetraazabicyclo[3.3.0] octanes" J. Phys. Chem. 90, 2679.

Bulusu, S. N., ed. (1990) Chemistry and Physics of Energetic Materials, Kluwer, Dordrecht, The Netherlands.

Cassar, L., Eaton, P. E. and Halpern, J. (1970) "Catalysis of Symmetry-Restricted Reactions by Transition Metal Compounds. The Valence Isomerization of Cubane." J. Am. Chem. Soc. 92, 3515.

Clabo, D. A. and Schaefer, III, H. F. (1987) "Fluorine Peroxide (FOOF): A Continuing Problem for Normally Reliable Theoretical Methods" Int. J. Quantum Chem. 31, 429.

Coffin, J. M. and Pulay, P. (1991) "An *Ab Initio* Study of Nitrous Acid: Geometries, Force Constants, Fundamental Frequencies, and Potential Surface for Cis-Trans Isomerization" J. Phys. Chem. 95, 118.

Correl, T., Larsen, N. W. and Pedersen, T. (1980) "Equilibrium Configuration and Barriers of Four Fluorine Substituted Nitrobenzenes, Obtained by Microwave Spectroscopy." J. Mol. Struct. 65, 43.

Cox, J. R. and Hillier, I. H. (1988) "*Ab Initio* Studies of the Decomposition of Energetic Materials. I. Hydrogen Transfer in TNT and in Model Systems." Chem. Phys. 124, 39.

Crampton, M. R. and Wilson, P. M. (1980) "The Stabilities of Meisenheimer Complexes. Part 22. The Ionization of 2,4-Dinitroaniline, its N-Alkylated Derivatives, and 2,6-Dinitroaniline in Methanol-Dimethyl Sulphoxide containg Sodium Methoxide" J. Chem. Soc., Perkin Trans. II, 1854.

Cromwell, N. H. and Graff, M. A. (1952) "Three-Ring Carbonyl Hyperconjugation in Cis and Trans Aryl-Aroyl Ethylene Imines and Related Compounds" J. Org. Chem. 17, 414.

Dacons, J. C., Adolph, H. G. and Kamlet, M. J. (1970) "Some Novel Observations Concerning the Thermal Decomposition of 2,4,6-Trinitroluene." J. Phys.Chem. 74, 3035.

Dewar, M. J. S. (1979) Bull. Soc. Chim. Belg. "σ-Conjugation and σ-Aromaticity" 88, 957.

Dewar, M. J. S. (1984) "Chemical Implications of σ Conjugation" J. Am. Chem. Soc. 106, 669.

Doyle, M. P. (1992) "Glossary of terms used in physical organic chemistry" Chemistry International 14, 12.

Engelke, R. and Stine, J. R. (1990) "Is N_8 Cubane Stable?" J. Phys. Chem. 94, 5689.

Engelke, R. (1989) "Five Stable Points on the N_6 Energy Hypersurface: Structures, Energies, Frequencies and Chemical Shifts" J. Phys. Chem. 93, 5722.

Engelke, R. (1990) "Reply to Comments on the Stable Points on the N_6 Energy Hypersurface" J. Phys. Chem. 94, 6924.

Exner, O. (1988) Correlation Analysis of Chemical Data, Plenum Publishing Corporation and
    SNTL Publishers of Technical Literature, Prague, Czechoslovakia.

Fliszár, S. (1980) "Charge Distributions and Chemical Effects. 23. The Chemical Bond, a Theory
    of Electron Density" J. Am. Chem. Soc. 102, 6946.

Gibson, B. and Crampton, M. R. (1979) "The Stabilities of Meisenheimer Complexes. Part 17.
    The Reactions of 1-X-2,4,6-Trinitrobenzenes with Hydroxide Ions in Water" J. Chem.
    Soc., Perkin Trans. II, 648.

Greenberg, A. and Liebman, J. F. (1978) Strained Organic Molecules; Academic Press: New
    York.

Griffin, G. W. and Marchand, A. P. (1989) "Synthesis and Chemistry of Cubanes" Chem. Rev.
    89, 997.

Grodzicki, M., Seminario, J. M. and Politzer, P. (1990) "Conformation-Dependent Effects of the
    Nitro Group Upon Some Strained Tertiary C-C Bonds" J. Phys. Chem., 94, 624.

Grodzicki, M., Seminario, J. M. and Politzer, P. (1990) "Computational Analysis of Some
    Possible Initial Steps in the Unimolecular Thermal Decompositions of 1,3-Diazacyclo-
    butane and its 1,3-Dinitramine Derivative" Theoret. Chim. Acta, 77, 359.

Grodzicki, M., Seminario, J. M. and Politzer, P, (1991) "Energy Barriers of Symmetry-Forbidden
    Reactions: Local Density Functional Calculations" J. Chem. Phys. 94, 1668.

Habibollahzadeh, D., Grodzicki, M., Seminario, J. M. and Politzer, P. (1991) "A Computational
    Study of the Concerted Triple Dissociations of 1,3,5 -Triazacyclohexane and its 1,3,5-
    Trinitro Derivative (RDX)" J. Phys. Chem., 95, 7699.

Habibollahzadeh, D., Murray, J. C., Redfern, P. C. and Politzer, P. (1991) "A Computational
    Study of the N-NO$_2$ Rotational Energy Barriers in Some Aliphatic and Alicyclic
    Nitramines" J. Phys. Chem., 95, 7702.

Habibollahzadeh, D., Murray, J. C., Grice, M. E. and Politzer, P. (1992) "X-NO$_2$ Rotational
    Energy Barriers: Local Density Functional Calculations" Int. J. Quantum Chem.,
    submitted.

Hammett, L. P. (1970) Physical Organic Chemistry, McGraw-Hill, New York.

Hehre, W. J., Ditchfield, R., Radom, L. and Pople, J. A. (1970) "Molecular Orbital Theory of the
    Electronic Structure of Organic Compounds. V. Molecular Theory of Bond Separation"
    J. Am. Chem. Soc. 92, 4796.

Hehre, W. J., Radom, L., Schleyer, P. v. R. and Pople, J. A. (1986) Ab Initio Molecular Orbital
    Theory, John Wiley and Sons, New York.

Hiberty, P. C. and Ohanessian, G. (1984) "Valence-Bond Description of Conjugated Molecules.
    3. The Through-Resonance Concept in Para-Substituted Nitrobenzenes." J. Am. Chem.
    Soc. 106, 6963.

Hinchliffe, A. (1988) Computational Quantum Chemistry, John Wiley and Sons, New York, Chap. 5.

Høg, J. N., Nygaard, L. and Sorensen, G. O. (1971) "Microwave Spectrum and Planarity of Nitrobenzene." J. Mol. Struct. 7, 111.

Iyer, S. and Slagg, N. (1988) "Molecular Aspects in Energetic Materials." Structure and Reactivity (Molecular Structure and Energetics), Liebman, J. F. and Greenberg, A., eds., VCH Publishers, New York, chap 7.

Kamlet, M. J. and Adolph, H. G. (1979) "The Relationship of Impact Sensitivity with Structure of Organic High Explosives. II. Polynitroaromatic Explosives." Propellants Explos. Pyrotech 4, 30.

Kamlet, M. J. and Adolph, H. G. (1981) "Some Comments Regarding the Sensitivities, Thermal Stabilities, and Explosive Performance Characteristics of Fluorodinitromethyl Compounds" Seventh Symposium on Detonation, Office of Naval Research, Washington, DC, pp. 84-92.

Kintzinger, J. P., Lehn, J. M. and Williams, R. L. (1969) "Nuclear relaxation and molecular properties. Part II. ^{14}N nuclear quadrupolar relaxation, ^{1}H line shapes and electron distribution in $X-NO_2$ compounds." Mol. Phys. 17, 135.

Kryachko, E. S. and Ludeña, E. V., eds. (1990) Energy Density Functional Theory of Many-electron Systems, Kluwer, Dordrecht, The Netherlands.

Labanowski, J. K. and Andzelm, J. W., eds. (1991) Density Functional Methods in Chemistry, Springer-Verlag, New York.

Lipkowitz, K. B. (1982) "A Reassessment of Nitrobenzene Valence Bond Structures." J. Am. Chem. Soc. 104, 2647.

March, J. (1985) Advanced Organic Chemistry, John Wiley & Sons, New York.

Marchand, A. P. (1989) "Synthesis and Chemistry of Homocubanes, Bishomocubanes and Trishomocubanes" Chem. Rev. 89, 1011.

Magers, D. H., Salter, E. A., Bartlett, R. J., Salter, C., Hess, B. A. and Schaad, L. J. (1988) "Do Stable Isomers of N_3H_3 Exist?" J. Am. Chem. Soc. 110, 3435.

Meyer, R., Gammeter, A., Smith, P., Kühne, H., Nösberger, P. and Günthard, H. H. (1973) "Torsion of the Nitro Group in Nitroethylene." Mol. Spectry. 46, 397.

Meyer, R. (1987) Explosives, VCH Publishers, Weinheim, Germany.

Mulliken, R. S. (1955) "Electron Population Analysis on LCAO-MO Molecular Wave Functions. I." J. Chem. Phys. 23, 1833.

Murray, J. S., Redfern, P. C., Seminario, J. M. and Politzer, P. (1990) "Anomalous Energy Effects in Some Aliphatic and Alicyclic Aza Systems and Their Nitro Derivatives" J. Phys. Chem., 94, 2320.

Murray, J. S., Seminario, J. M., Lane, P. and Politzer, P. (1990) "Anomalous Energy Effects Associated with the Presence of Aza Nitrogens and Nitro Substitutents in Some Strained Systems" J. Mol. Struct. (Theochem), 207, 193.

Murray, J. S., Lane, P., Politzer, P. and Bolduc, P. R. (1990) "A Relationship between Impact Sensitivity and the Electrostatic Potentials at the Midpoints of $C-NO_2$ Bonds in Nitroaromatics," Chem. Phys. Lett. 168, 135.

Murray, J. S., Lane, P., Politzer, P., Bolduc, P. R. and McKenney, R. L., Jr. (1990) "A Computational Analysis of Some Possible Hydrogen Transfer and Intramolecular Ring Formation Reactions of o-Nitrotoluene and o-Nitroaniline" J. Mol. Struct. (Theochem), 209, 349.

Murray, J. S., Sukumar, N., Ranganathan, S. and Politzer, P. (1990)"A Computational Analysis of the Electrostatic Potentials and Relative Bond Strengths of Hydrazine and Some of its 1,1-Dimethyl Derivatives" Int. J. Quantum Chem., 37, 611 (1990).

Murray, J. S., Redfern, P. C., Lane, P., Politzer, P. and Willer, R. L. (1990) "A Computational Study of Structural and Reactive Properties of Imidazolidine, Piperazine, and Their N,N-Dinitro Derivatives" J. Mol. Struct. (Theochem), 207, 177.

Murray, J. S. and Politzer, P. (1991) "Correlations Between the Solvent Hydrogen-Bond-Donating Parameter α and the Calculated Molecular Surface Electrostatic Potential." J. Org. Chem. 56, 6715.

Murray, J. S. and Politzer, P. (1992) "Relationships between Solute Hydrogen-bond Acidity/Basicity and the Calculated Electrostatic Potential." J. Chem. Res. (S), 110.

Murray, J. S., Lane, P. and Politzer, P. (1992) "Relationships between Calculated Surface Electrostatic Potentials and Impact/Shock Sensitivities of Nitroaromatics and Nitramines", in preparation.

Murray, J. S., Seminario, J. M. and Politzer, P. (1991) "Effects of the Simultaneous Presence of Nitro and Amine Substituents in Cubane and Some Azacubanes" Structural Chem., 2, 153.

Murray, J. S., Concha, M., Seminario, J. M. and Politzer, P. "A Computational Study of Relative Bond Strengths and Stabilities of a Series of Amine and Nitro Derivatives of Triprismane and Some Azatriprismanes" (1991) J. Phys. Chem., 95, 1601.

Murray, J. S., Seminario, J. M. and Politzer, P. "Effect of the Amine Group on Relative Bond Strengths in Cubane and Azacubanes" Struct. Chem., in press.

Neilsen, A. T., Chafin, A. P. and Christian, S. L. (1984) "Nitrocarbons. 4 Reaction of Polynitrobenzenes with Hydrogen Halides. Formation of Polynitrohalobenzenes" J. Org. Chem. 49, 4575.

Owens, F. J. (1984) "Relationship Between Impact Induced Reactivity of Trinitroaromatic Molecules and Their Molecular Structure." J. Mol. Struct. (Theochem) 121, 213.

Owens, F. J., Jayasuriya, K., Abrahmsen, L. and Politzer, P. (1985) "Computational Analysis of Some Properties Associated with the Nitro Groups in Polynitroaromatic Molecules." Chem. Phys. Lett. 116, 434.

Paquette, L. A., Boggs, R. A. and Ward, J. S. (1975) "Rhodium (I)- and Palladium (II)-Promoted Rearrangement of Homocubanes. A Comparison of Kinetic Reactivity and Product Distribution with Substituted Alteration." J. Am. Chem. Soc. 97, 1118.

Parr, R. G. and Yang, W. (1989) Density Functional Theory of Atoms and Molecules, Oxford Univ. Press.

Politzer, P. and Daiker, K. C. (1981) "Models for Chemical Reactivity." The Force Concept in Chemistry, B. M. Deb, ed., Van Nostrand Reinhold Co., New York, ch. 6.

Politzer, P. and Truhlar, D. G. eds. (1981) Chemical Applications of Atomic and Molecular Electrostatic Potentials, Plenum Press, New York.

Politzer, P., Domelsmith, L. N., Sjoberg, P. and Alster, J. (1982) "Electrostatic Potentials of Strained Systems: Nitrocyclopropane" Chem. Phys. Letters, 92, 366.

Politzer, P., Domelsmith, L. N. and Abrahmsen, L. (1984) "Electrostatic Potentials of Strained Systems: Cubane, Homocubane and Bishomocubane" J. Phys. Chem. 88 1752.

Politzer, P., Abrahmsen, L. and Sjoberg, P. (1984) "The Effects of Amine and Nitro Substituents upon the Electrostatic Potential of an Aromatic Ring." J. Amer. Chem. Soc.106, 855.

Politzer, P., Sukumar, N., Jayasuriya K. and Ranganathan, S. (1988) "A Computational Evaluation and Comparison of Some Nitramine Properties" J. Amer. Chem. Soc., 110, 3425.

Politzer, P., Kirschenheuter, G. P. and Alster, J. (1987) "The Effects of Various Substituents Upon the Properties of the Bond Between the Bridgehead Carbons in Bicyclobutane" J. Amer. Chem. Soc. 109, 1033.

Politzer, P., Bar-Adon, R. and Miller, R. S. (1987) "A Comparative Analysis of O-O Bond Properties in Dioxirane, Hydrogen Peroxide and Peroxytrifluoroacetic Acid" J. Phys. Chem. 91, 3191.

Politzer, P. and Murray, J. S. (1988) "Bond Deviation Indices and Electrostatic Potentials of Some Strained Hydrocarbons and Their Derivatives" in Molecular Structure and Energetics, Vol 7, J. F. Liebman and A. Greenberg, eds., VCH Publishers, New York, Ch. 1.

Politzer, P., Seminario, J. M. and Bolduc, P. R. (1989)"A Proposed Interpretation of the Destabilizing Effect of Hydroxyl Groups on Nitroaromatic Molecules" Chem. Phys. Lett., 158, 463.

Politzer, P. and Seminario, J. M. (1989) "A Computational Determination of the Structures and Some Properties of Tetrahedrane, Prismane and Some of Their Aza Analogs" J. Phys. Chem., 93, 588.

Politzer, P. and Seminario, J. M. (1990) "Calculated Structures, Relative Energies and Electrostatic Potentials of Some Tetraaza Cyclic Systems" Struct. Chem., 1, 325.

Politzer, P. and Murray, J. S. (1991) "Molecular Electrostatic Potentials and Chemical Reactivity." Reviews in Computational Chemistry, Lipkowitz, K. B. and Boyd, D. B. eds., VCH Publishers, New York, Ch. 7.

Politzer, P. Murray, J. S. Lane, P. Sjoberg, P. and Adolph, H. G. (1991) "Shock Sensitivity Relationships for Nitramines and Nitroaliphatics" Chem. Phys. Letters, 181, 78.

Politzer, P. and Murray, J. S. (1992) "General and Theoretical Aspects of the -OH, -O- and -O-O- Groups Integration of Theory and Experiment" in Supplement E2: Chemistry of Hydroxyl, Ether and Peroxide Groups, John Wiley & Sons, Chichester, England.

Politzer, P., Murray, J. S., Seminario, J. M.and Miller, R. S. (1992) "Computational Analysis of Dinitramine and Chlorine Derivatives of Benzene and s-Tetrazine" J. Mol. Struct. (Theochem), in press.

Ritchie, J. P. (1988) "A Look at Mesomerism in Nitrobenzene." Tetrahedron 24, 7465.

Rogers, R. N. (1967) "Combined Pyrolysis and Thin Layer Chromotography: A Method for the Study of Decomposition Mechanisms." Anal. Chem. 39, 730.

Saxon, R. P. and Yoshimine, M. (1989) "Theoretical Study of Nitro-Nitrite Rearrangement of NH_2NO_2" J. Phys. Chem. 93, 3130.

Scrocco, E. and Tomasi, J. (1978) "Electronic Molecular Structure, Reactivity and Intermolecular Forces: A Heuristic Interpretation by Means of Molecular Electrostatic Potentials." Adv. Quantum Chem., 11, 115.

Seminario, J. M. and Politzer, P. (1992) "Gaussian-2 and Density Functional Studies of H_2N-NO_2 Dissociation, Inversion and Isomerization" Int. J. Quantum Chem., Quantum Chem. Symp. 26, in press.

Seminario, J. M., Grodzicki, M. and Politzer, P. (1991) "Application of Local Density Functional Theory to the Study of Chemical Reactions" in Density Functional Methods in Chemistry, J. K. Labanowski and J. W. Andzelm, eds., Springer-Verlag, New York, ch. 28.

Seminario, J. M., Concha, M. C. and Politzer, P. (1992) "Calculated Structures and Relative Stabilities of Furoxan, Some 1,2-Dinitrosoethylenes and Other Isomers" J. Comput. Chem., 13, 177.

Shackelford, S. A., Beckmann, J. W. and Wilkes, J. S. (1977) "Deuterium Isotope Effects in the Thermal Decomposition of Liquid 2,4,6-Trinitrotolutene: Application to Mechanistic Studies Using Isothermal Differential Scanning Calorimetry Analysis." J. Org. Chem. 42, 4201.
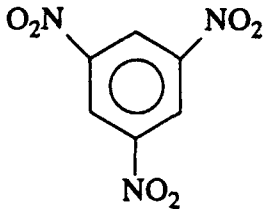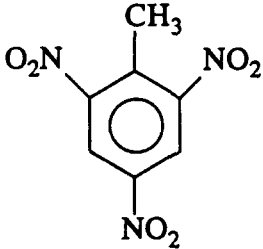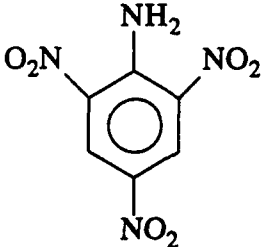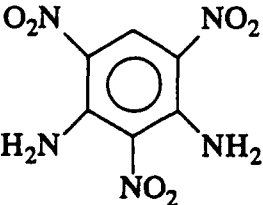
Sharma, J., Hoffsomer, J. C., Glover, D. J., Coffey, C. S., Santiago, F., Stolovy, A. and Yasuda, S. (1983) "Comparative Study of Molecular Fragmentation in Sub-Initiated TATB Caused by Impact, UV, Heat and Electron Beams." Shock Waves in Condensed Matter, Graham, R. A. and Straub, G. K., eds., Elsevier, Amsterdam, pp. 543-546.

Sharma, J. Forbes, J. W., Coffey, C. S. and Liddiard, T. P. (1987) "The Physical and Chemical Nature of Sensitization Centers Left from Hot Spots Caused in Triaminotrinitrobenzene by Shock or Impact." J. Phys. Chem. 91, 5139.

Sjoberg, P. and Politzer, P. (1990) "The Use of the Electrostatic Potential at the Molecular Surface to Interpret and Predict Nucleophilic Processes." J. Phys. Chem., 94, 3959.

Sjoberg, P., Murray, J. S., Brinck, T. and Politzer, P. (1990) "Average Local Ionization Energies on the Molecular Surfaces of Aromatic Systems as Guides to Chemical Reactivity." Can. J. Chem., 68, 1440.

Stewart, P. H., Jeffries, J. B., Zellweger, J. -M., McMillen, D. F. and Golden, D. M. (1989) "Molecular Beam Sampled Laser Pyrolysis of Dimethylnitramine" 93, 3557.

Stine, J. R. (1989) J. Energetic Materials.

Storm, C. B., Ryan, R. R., Ritchie, J. P., Hall, J. H. and Bachrach, S. M. (1989) "Structural Basis of the Impact Sensitivities of 1-Picryl-1,2,3-triazole, 2-Picryl-1,2,3-triazole, 4-Nitro-1-picryl-1,2,3-triazole, and 4-Nitro-2-picryl-1,2,3-triazole." J. Phys. Chem. 93, 1000.

Storm, C. B., Stine, J. R. and Kramer, J. F. (1990) "Sensitivity Relationships in Energetic Materials." Chemistry and Physics of Energetic Materials, Bulusu, S. N., ed., Kluwer, Dordrecht, The Netherlands, Chap. 27.

Thomas, J. R., Quelch, G. E. and Schaefer III, H. F. (1991) "The Unknown Unsubstituted Tetrazines: 1,2,3,4-Tetrazine and 1,2,3,5-Tetrazine." J. Org. Chem. 56, 539.

Turner, A. G. and Davis, L. P. (1984) "Thermal Decomposition of TNT: Use of 1-Nitropropene to Model the Initial Stages of Decomposition." J. Am. Chem. Soc. 106, 5447.

Wiberg, K. B. (1965) "Bicyclo[1.1.0] butane." Rec. Chem. Prog. 26, 143.

Zhao, X., Hintsa, E. J. and Lee, Y. T. (1987) "Infrared multiphoton dissociation of RDX in a molecular beam" J. Chem. Phys. 88, 801.

Table 1. Measured impact and shock sensitivities of some common explosives.[a]

Molecule	Impact drop height[b] (cm)	P_{90}[c] (kbar)
O_2N—O—H_2C CH_2—O—NO_2 \ C / O_2N—O—H_2C CH_2—O—NO_2 **1, PETN**	12	7.47
CH_2—O—NO_2 | CH—O—NO_2 | CH_2—O—NO_2 **2, nitroglycerin**	20	---
4, RDX	24	10.97
7, HMX	26	10.81
5, Tetryl	32	10.64

(continued)

Table 1. Measured impact and shock sensitivities of some common explosives (continued).[a]

Molecule	Impact drop height[b] (cm)	P_{90}[c] (kbar)
3, TNB	100	14.96
8, TNT	160	17.72
9, MATB	177	27.91
10, TATB	320	46.20

[a]Data taken from Storm, Stine and Kramer, 1990.

[b]The impact sensitivity as impact drop height as measured at the Los Alamos National Laboratory and/or Naval Surface Warfare Center using the Bruceton Method, type 12 tools, 2.5 kg weight, 40 mg sample, 5/0 sandpaper, 25 trials. Impact sensitivity increases as impact drop height decreases.

[c]The shock sensitivity as measured by the Naval Surface Warfare Center small scale gap test; P_{90} is the pressure to 90% of its theoretical maximum density. Shock sensitivity increases as P_{90} increases.

Table 2. Calculated and experimental geometries.[a]

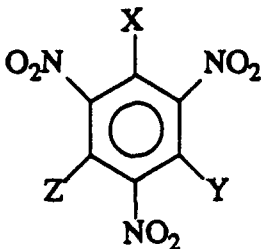| Molecule	Structural parameter	HF/STO-3G	HF/3-21G	HF/6-31G*	MP2/6-31G*	DFT-local	DFT-nonlocal	Experimental
CH_3NO_2	r(CN)	1.530	1.492	1.479	1.486	1.477c	1.511c	1.489d
	r(NO)	1.275, 1.276	1.239, 1.242	1.191, 1.192	1.240, 1.241	1.230, 1.230c	1.246, 1.246c	1.224d
	∠(ONO)	124.8	121.2	123.9	125.7	125.8c	125.5c	125.3d
NH_2NO_2[b]	r(NN)	1.472	1.354	1.356	1.399	1.371	1.416	1.427e, 1.381f
	r(NO)	1.273	1.247	1.191	1.233	1.230	1.244	1.206e, 1.232f
	∠(ONO)	127.4	127.2	127.0	127.7	127.4	127.4	130.1e, 132.7f
	∠(HNH)	105.1	128.0	116.7	114.3	119.6	115.1	115.2e, 109.7f
	∠(HNNO)	33.8	0.0	25.7	29.5	22.9	28.6	26.5e, 22.5f
(benzene ring)	r(CC)	1.387	1.385	1.386	1.395	1.385	1.408c	1.396d
(nitrobenzene ring, NO_2)	r(C1C2)	1.378	1.378	1.383	---	---	---	1.391, (C-C)ave[g]
	r(C2C3)	1.386	1.381	1.383	---	---	---	---
	r(C3C4)	1.389	1.385	1.387	---	---	---	---
	r(CN)	1.507	1.449	1.459	---	---	---	1.492g
	r(NO)	1.278	1.244	1.194	---	---	---	1.226g
	∠(ONO)	124.1	124.8	124.6	---	---	---	124.4g

[a]Bond distances and angles are in units of Å and degrees, respectively. Unless otherwise indicated the calculated geometries have been computed for the purposes of this or earlier work. [b]Calculated data have been taken from Seminario, J. M. and Polizer, P. (1992) Int. J. Quantum Chem., Quant. Chem. Symp. 26, in press. [c]J. M. Seminario and P. Polizer, unpublished work. [d]Harmony, M. D.; Laurie, V. W., Kuszkowski, R. L., Schwendeman, R. H., Ramsay, D. A., Lovas, F. J., Lafferty, W. J. and Maki, A. G. (1979) J. Phys. Chem. Ref. Data 8, 619. [e]Tyler J. K. (1963) J. Mol. Spectrosc. 11, 39. [f]Sadova, N. I., Slepnev, G. E., Tarasenko, N. A., Zenkin, A. A., Vilkov, L. V., Pankrushev, I. F. and Yu, A. (1977) Zh. Strukt. Khim. 18, 865. [g]Högg, J. H., Nygaard, L. and Sorensen, G. O. (1971). J. Mol. Struct. 7, 111.

Table 3. Some calculated and experimental molecular properties.[a]

Molecule	Π (kcal/mole)	μ (Debye)	ε
$c\text{-}C_6H_{12}$	2.2	0.0	2.02
$C_6H_5CH_3$	4.6	0.36	2.38
CCl_4	4.8	0.0	2.24
C_6H_6	4.9	0.0	2.28
$C_6H_5CCH_3$	7.2	3.02	17.39
C_6H_5Cl	8.0	1.69	5.71
C_6H_5OH	8.6	1.45	9.78
CH_3COCH_3	9.4	2.88	20.7
C_2H_5OH	10.1	1.69	24.3
$C_6H_5NO_2$	12.3	4.22	34.82
CH_3COOH	12.9	1.74	6.15
$p\text{-}C_6H_4(NO_2)_2$	16.5	0.00	---
CH_3CN	17.1	3.92	36.2
$(CH_3)_2SO$	19.1	3.96	46.60
CH_3NO_2	19.9	3.46	35.9
H_2O	21.6	1.85	78.54

[a]These calculated Π values and experimentally determined dipole moments μ and dielectric constants ε are taken from Brinck et al [1992].

Table 4. Calculated and experimentally-determined properties for some trinitroaromatics.

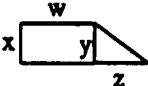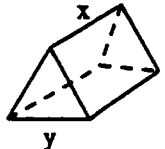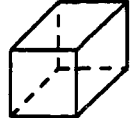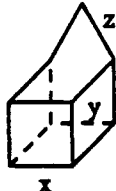| X, Y, Z	Impact drop height[a] (cm)	$V_{mid,max}$[b] (kcal/mole)	Π[c] (kcal/mole)	Ring center $V_{S,max}$[d] (kcal/mole)
H, NO$_2$, H	---	142.4	21.4	52
1,2,4,5-tetranitro	27	141.8	21.4	50
NH$_2$, NO$_2$, H	41	150.6	21.2	46 NH$_2$: 42
Cl, H, H	79	146.8	19.1	45
OH, H, H	87	127.4	21.0	OH: 58 39
H, H, H	100	130.5	19.5	39
COOH, H, H	109	128.6	19.5	COOH: 43 41
CH$_3$, H, H	160	131.1	18.2	37
NH$_2$, H, H	177	109.2	18.6	36 NH$_2$: 32
OCH$_3$, H, H	192	117.3	18.2	40
OCH$_3$, OCH$_3$, H	251	116.1	17.6	38
NH$_2$, NH$_2$, H	320	91.6	17.1	33
NH$_2$, NH$_2$, NH$_2$	>320	64.6	16.1	31

[a]The impact sensitivity as impact drop height as measured at the Los Alamos National Laboratory and/or Naval Surface Warfare Center using the Bruceton Method, type 12 tools, 2.5 kg weight, 40 mg sample, 5/0 sandpaper, 25 trials. Impact sensitivity increases as impact drop height decreases.

[b]Data taken from Murray, Lane, Politzer and Bolduc, 1990; units have been converted to kcal/mole.

[c]Data taken from Murray, Lane, Brinck and Politzer, 1992.

[d] The $V_{S,max}$ are located above or below the aromatic ring unless otherwise indicated.

Table 5. Calculated bond deviation indices[a] and isodesmic reaction energies[b] of some hydrocarbons.

Molecule	Bond deviation index	$\Delta E_{isodesmic}$ (kcal/mole)
$CH_3CH_2CH_3$	0.000	-1.4[c]
	0.080	31.4
	0.023	23.4
	x: 0.084 y: 0.080	---
	0.116	151.0
	w: 0.023 x: 0.022 y: 0.081 z: 0.078	---
	x: 0.033 y: 0.080	140.3
	0.029	127.0
	x: 0.030 y: 0.020 z: 0.009	---

[a]Taken from Politzer and Murray, 1988.

[b]HF/3-21G results taken from Murray, Lane, Seminario and Politzer, 1990, unless otherwise indicted.

[c]HF/3-21G results taken from Murray, Redfern, Seminario and Politzer, 1990.
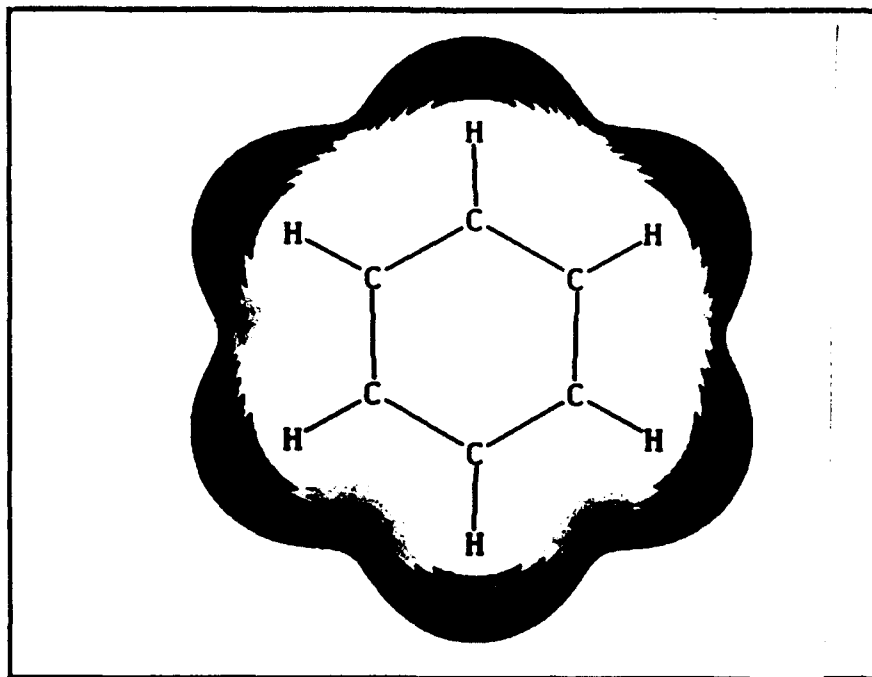
Figures Captions

Figure 1. Calculated HF/STO-5G electrostatic potential on the molecular surface of benzene. Two ranges of V(r) are depicted; these are, in kcal/mole: white < 0; 0 < gray < 10.

Figure 2. Calculated HF/STO-5G electrostatic potential on the molecular surface of nitrobenzene. Three ranges of V(r) are depicted; these are, in kcal/mole: white < 0; 0 < gray < 10; 10 < black.

Figure 3. Calculated HF/STO-5G electrostatic potential on the molecular surface of 1,3,5-trinitrobenzene. Three ranges of V(r) are depicted; these are, in kcal/mole: white < 0; 0 < gray < 35; 35 < black.

Figure 1.   Calculated HF/STO-5G electrostatic potential on the molecular surface of benzene. Two ranges of V(r) are depicted; these are, in kcal/mole: white < 0; 0 < gray < 10.
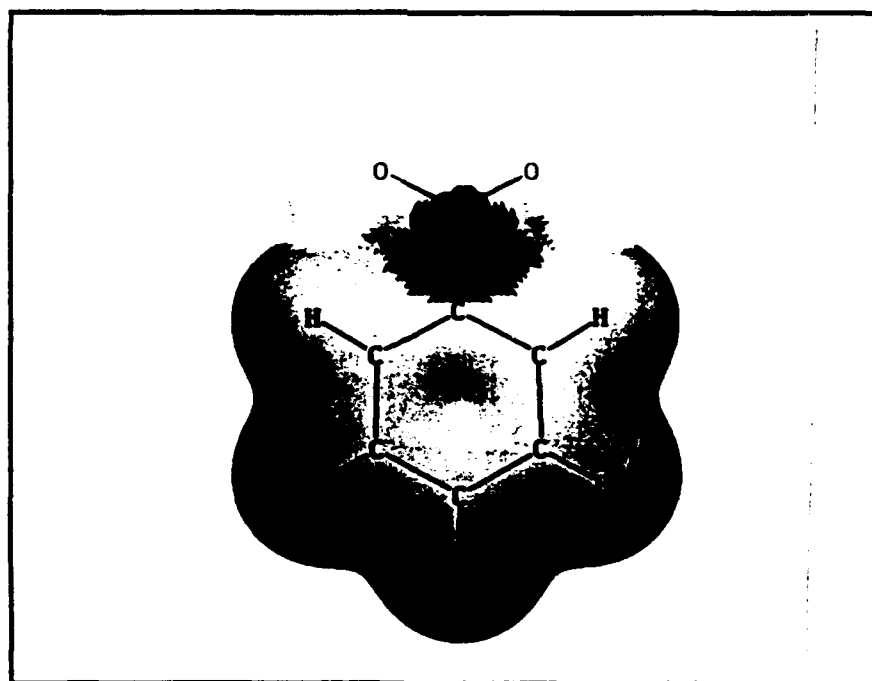

Figure 2.   Calculated HF/STO-5G electrostatic potential on the molecular surface of nitrobenzene. Three ranges of V(r) are depicted; these are, in kcal/mole: white < 0; 0 < gray < 10; 10 < black.

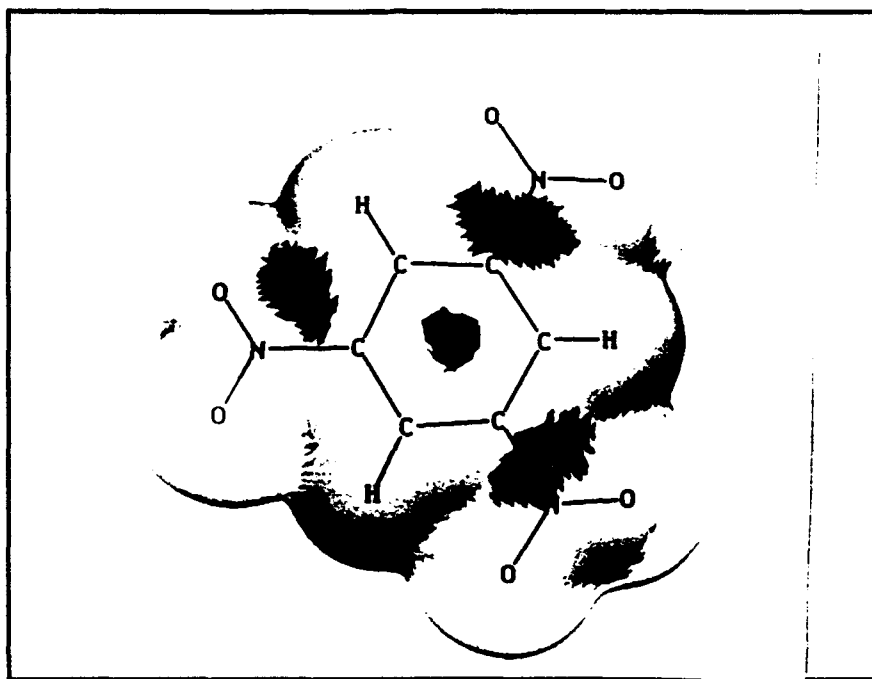Figure 3. Calculated HF/STO-5G electrostatic potential on the molecular surface of 1,3,5-trinitrobenzene. Three ranges of V(r) are depicted; these are, in kcal/mole: white < 0; 0 < gray < 35; 35 < black.